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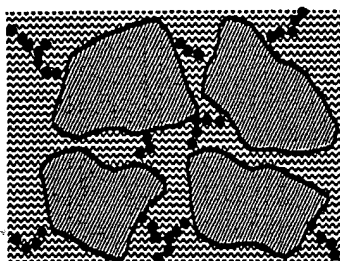
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(54) Matériaux d'électrode présentant une conductivité de surface élevée

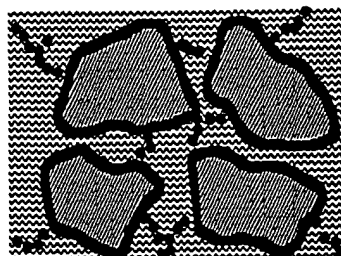
(57) La présente invention concerne les matériaux d'électrode capables de réaction rédox par échange d'ions alcalins et d'électrons avec un électrolyte. Les ap-

plications sont dans le domaine des générateurs électrochimiques (batteries) primaires ou secondaires, les supercondensateurs et les systèmes de modulation de la lumière de type supercondensateur.

FIGURE 1



a)



b)

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de cycles. Ces contraintes, ou stress, chimiques et mécaniques se traduisent au niveau microscopique par une désintégration des grains de matériau électroactif, dont une partie est susceptible de perdre le contact avec les grains de carbone et de devenir ainsi inactifs électrochimiquement. La structure du matériau peut aussi être détruite, avec l'apparition de nouvelles phases et relargage éventuel des dérivés ou autres fragments de métaux de transition dans l'électrolyte. Ces phénomènes nuisibles apparaissent d'autant plus facilement lorsque la densité de courant ou la puissance demandée à l'électrode est plus grande.

DANS LES DESSINS

10 [0006] La Figure 1 illustre la différence entre une électrode classique selon l'art antérieur (A) et une électrode selon l'invention dont les particules de matériau électroactif sont recouvertes d'un revêtement carboné (B).

[0007] Les Figures 2 et 3 illustrent une comparaison d'un échantillon de LiFePO_4 recouvert de carbone avec un échantillon témoin de LiFePO_4 sans carbone. Ces résultats ont été obtenus par voltammétrie cyclique de piles LiFePO_4 / $\text{POE}_{20}\text{LiTFSI}$ / Li cyclées à 20 mV.h^{-1} entre 3 et 3.7 volts à 80°C . Le premier cycle est porté sur la Figure 2 et le cinquième sur la Figure 3.

[0008] La Figure 4 illustre l'évolution de la capacité au cours du cyclage des piles réalisées avec l'échantillon de LiFePO_4 carboné d'une part et le témoin non carboné d'autre part.

[0009] La Figure 5 illustre les performances d'une pile contenant LiFePO_4 carboné et cyclée en mode intensostatique entre 3 et 3.8 Volts à 80°C avec une vitesse de charge et décharge correspondant à C/1.

20 [0010] La Figure 6 illustre l'évolution du courant en fonction du temps d'une pile LiFePO_4 / γ -butyrolactone LiTFSI / Li contenant un échantillon carboné et cyclé à 20 mV.h^{-1} entre 3 et 3.7 volts à température ambiante.

[0011] La Figure 7 illustre l'évolution du courant en fonction du temps d'une pile LiFePO_4 / $\text{POE}_{20}\text{LiTFSI}$ / Li contenant un échantillon carboné.

25 [0012] Les Figures 8-9 présentent une comparaison d'échantillons de LiFePO_4 recouverts de carbone avec un échantillon témoin de LiFePO_4 avant traitement. Ces résultats ont été obtenus par voltammétrie cyclique de piles LiFePO_4 / $\text{POE}_{20}\text{LiTFSI}$ / Li cyclées à 20 mV.h^{-1} entre 3 et 3.7 volts à 80°C . Le premier cycle est illustré sur la Figure 8 et le cinquième sur la Figure 9.

[0013] La Figure 10 illustre l'évolution de la capacité au cours du cyclage des piles réalisées avec les échantillons de LiFePO_4 carbonés d'une part et le témoin non carboné d'autre part.

SOMMAIRE DE L'INVENTION

30 [0014] La présente invention concerne un matériau d'électrode comprenant un oxyde complexe correspondant à la formule générale $\text{A}_a\text{M}_m\text{Z}_z\text{O}_o\text{N}_n\text{F}_f$ dans laquelle:

A comprend un métal alcalin;

M comprend au moins un métal de transition, et optionnellement un métal autre qu'un métal de transition, tel que le magnésium ou l'aluminium; ou leurs mélanges;

Z comprend au moins un non-métal;

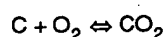
40 O est l'oxygène; N l'azote et F le fluor; et

les coefficients a, m, z, o, n, f ≥ 0 étant choisis de manière à assurer l'électroneutralité, caractérisé en ce qu'un dépôt de matériau carboné conducteur est déposé à la surface du matériau d'une manière homogène de façon à obtenir une distribution substantiellement régulière du champ électrique à la surface des grains du matériau. La similarité des rayons ioniques entre l'oxygène, le fluor et l'azote permet le remplacement mutuel de ces éléments en autant que l'électroneutralité est maintenue. Pour des raisons de simplification, et considérant que l'oxygène est utilisé le plus fréquemment, ces matériaux seront appelés des oxydes complexes. Les métaux de transition préférentiels comprennent le fer, le manganèse, le vanadium, le titane, le molybdène, le niobium, le zinc et le tungstène, seuls ou en mélanges. Les métaux autres qu'un métal de transition préférentiels comprennent le magnésium ou l'aluminium, et les non-métaux préférentiels comprennent le soufre, le sélénium, le phosphore, l'arsenic, le silicium, le germanium, le bore et l'étain, seuls ou en mélanges.

[0015] Dans une mise en œuvre préférentielle, la teneur massique finale en matériau carboné est comprise entre 0.1 et 55%, et plus préférentiellement entre 0.2 à 15%.

55 [0016] Dans une autre mise en œuvre préférentielle, l'oxyde complexe comprend les sulfates, phosphates, silicates, oxysulfates, oxyphosphates et xysilicates, ou leurs mélanges, d'un métal de transition et de lithium, et leurs mélanges. Il peut être intéressant, pour des raisons de stabilité structurale, de substituer partiellement le métal de transition par un élément de même rayon ionique mais inactif au point de vue redox. Par exemple, le magnésium et l'aluminium, dans des proportions préférentielles de 1 à 25%.

Une méthode préférée consiste à pyrolyser une matière organique, de préférence riche en carbone, en présence du matériau rédox. Sont particulièrement avantageux les mésomolécules et polymères susceptibles de former facilement, soit mécaniquement, soit par imprégnation à partir d'une solution ou par polymérisation *in situ*, une couche uniforme à la surface des grains du matériau rédox. Une pyrolyse ou déshydrogénation de l'ensemble permet d'obtenir une couche fine et uniforme de matériau carboné à la surface des grains du matériau rédox. Afin que la composition de ce dernier ne soit pas affectée par la réaction de pyrolyse ou de déshydrogénation, il est judicieux de choisir des compositions dont la pression d'oxygène libérée par le matériau soit suffisamment faible pour éviter l'oxydation du carbone formé par la pyrolyse. L'activité de l'oxygène des composés $A_m M_n Z_x O_y N_f$ peut être contrôlée par la teneur en métal alcalin, qui elle-même détermine l'état d'oxydation du ou des éléments de transition contenus dans le matériau et fait partie intégrale de l'invention. Sont particulièrement intéressants les compositions dans lesquelles le coefficient "a" de la teneur en métal alcalin permet de maintenir les états d'oxydation suivant: Fe^{2+} , Mn^{2+} , V^{2+} , V^{3+} , Ti^{2+} , Ti^{3+} , Mo^{3+} , Mo^{4+} , Nb^{3+} , Nb^{4+} , W^{4+} . D'une manière générale, des pressions d'oxygène de l'ordre 10^{-20} bars à $0^\circ C$ et de 10^{-10} bars à $900^\circ C$ sont suffisamment faibles pour permettre le dépôt de carbone par pyrolyse, la cinétique de formation de carbone en présence de résidu hydrocarbonés dus à la pyrolyse étant plus rapide et moins fortement activée que la formation d'oxygène à partir du matériau rédox. Il est aussi possible et avantageux de choisir des matériaux dont la pression d'oxygène en équilibre avec le matériau soit inférieure à celle de l'équilibre



[0024] Dans ce cas, le matériau carboné peut être thermodynamiquement stable vis-à-vis de l'oxyde complexe. Les pressions correspondantes sont obtenues par la formule suivante:

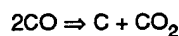
$$\ln P(O_2) = \ln P(CO_2) = \frac{94050}{R(273,2 + \theta)}$$

dans laquelle R est la constante des gaz parfaits ($1,987 \text{ cal.mole}^{-1} \cdot K^{-1}$); et θ est la température en $^\circ C$.

[0025] Le tableau suivant donne les valeurs des pressions d'oxygène pour quelques températures:

	$P(O_2)$	$P(O_2)$
$\theta (^\circ C)$	$P(CO_2) = 1 \text{ atm}$	$P(CO_2) = 10^{-5} \text{ atm}$
200	3.5×10^{-44}	3.5×10^{-49}
300	1.4×10^{-36}	1.4×10^{-41}
400	2.9×10^{-31}	2.9×10^{-36}
500	2.5×10^{-27}	2.5×10^{-32}
600	2.9×10^{-24}	2.5×10^{-29}
700	7.5×10^{-22}	7.5×10^{-27}
800	7.0×10^{-20}	7.0×10^{-25}
900	3.0×10^{-18}	3.0×10^{-23}

[0026] Il est aussi possible d'effectuer le dépôt carboné par la dismutation de l'oxyde de carbone à des températures inférieures à $800^\circ C$ selon l'équation:



[0027] Cette réaction est exothermique mais lente. Les particules d'oxyde complexe peuvent être mises en contact avec le monoxyde de carbone pur ou dilué par un gaz inerte, à des températures allant de 100 à $750^\circ C$, de préférence de 300 à $650^\circ C$. Avantageusement, la réaction est conduite en technique de lit fluidisé, de manière à avoir une grande surface d'échange entre la phase gazeuse et la phase solide. Les éléments et cations des métaux de transition présents dans l'oxyde complexe sont des catalyseurs de la réaction de dismutation. Il peut être intéressant d'ajouter des faibles quantités de métaux de transition, préférablement le fer, nickel, cobalt à la surface des grains, ces éléments étant particulièrement actifs comme catalyseur de la réaction de dismutation. On peut aussi faire appel à la décom-

culaire destiné à être imbibé d'électrolyte, soit conducteur par simple contact entre les particules. En général, ce comportement peut s'observer à des fractions volumiques comprises entre 10 et 70%.

[0037] Il peut être aussi avantageux de choisir des dépôts de matériau carboné suffisamment fin pour ne pas faire obstacle au passage des ions, tout en assurant la répartition du potentiel électrochimique à la surface du grain. Dans ce cas, les mélanges binaires ne possèdent éventuellement pas une conductivité électronique suffisante pour assurer les échanges électroniques avec le support de l'électrode (collecteur de courant). L'ajout d'un tiers composant conducteur électronique, sous forme de poudre fine ou de fibres, permet d'obtenir une conductivité macroscopique satisfaisante et améliore les échanges électroniques avec le support de l'électrode. Les noirs de carbone ou les fibres de carbone sont particulièrement avantageux pour cette fonction, et donnent des résultats satisfaisants à des taux volumiques n'affectant peu ou pas la rhéologie lors de la mise en œuvre de l'électrode du fait de l'existence d'une conductivité électronique à la surface des grains du matériau d'électrode. Des fractions volumiques de 0.5 à 10% sont particulièrement préférées. Les noirs de carbone de type noir de Shawinigan® ou Ketjenblack® sont préférés. Parmi les fibres de carbone, celles obtenues par pyrolyse de polymères tels que le brai, le goudron, le polyacrylonitrile ainsi que celles obtenues par "cracking" d'hydrocarbures sont préférées.

[0038] Il est intéressant, du fait de sa légèreté et de sa malléabilité, d'utiliser l'aluminium comme constituant des collecteurs de courant. Ce métal est néanmoins recouvert d'une couche isolante d'oxyde. Cette couche, qui protège le métal de la corrosion, peut dans certaines conditions augmenter d'épaisseur, ce qui amène une résistance accrue de l'interface, préjudiciable au bon fonctionnement de la cellule électrochimique. Ce phénomène peut être particulièrement gênant et rapide dans le cas où la conductivité électronique serait uniquement assurée, comme dans l'art antérieur, par des grains de carbone ayant un nombre de points de contacts limités. L'utilisation, en conjonction avec l'aluminium, des matériaux d'électrode recouverts d'une couche de matériau carboné conducteur permet d'augmenter la surface d'échange aluminium-électrode. Les effets d'une corrosion de l'aluminium sont ainsi annulés ou à tout le moins significativement minimisés. Il est possible d'utiliser soit des collecteurs d'aluminium sous forme de feuillets ou éventuellement sous forme de métal déployé ou expansé, ce qui permet un gain de poids. Du fait de propriétés des matériaux de l'invention, même dans le cas d'un métal déployé, les échanges électroniques au niveau du collecteur se font sans surcroît notable de la résistance.

[0039] Lorsque les collecteurs de courant sont thermiquement stables, il est aussi possible d'effectuer la pyrolyse ou déshydrogénation directement sur le collecteur, de manière à obtenir après dépôt de carbone, un film continu poreux qui peut être infiltré par un liquide conducteur ionique, ou bien par un monomère ou mélange de monomères dont la polymérisation *in situ* génère un électrolyte polymère. La formation de films poreux dans lesquels le revêtement carboné forme une trame sont aisément obtenus dans le cadre de l'invention par pyrolyse d'un composite polymère-oxyde complexe déposé à l'état de film sur un support métallique.

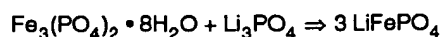
[0040] Lors de la mise en œuvre du matériau d'électrode de la présente invention dans une cellule électrochimique, préférablement de type batterie primaire ou secondaire, l'électrolyte est un préférablement un polymère, solvantant ou non, optionnellement plastifié ou gélifié par un liquide polaire contenant en solution un ou plusieurs sels métalliques, et préférablement au moins un sel de lithium. Dans un tel cas, le polymère est préférablement formé à partir d'unités oxyéthylène, oxypropylène, acrylonitrile, fluorure de vinylidène, des esters de l'acide acrylique ou métacrylique, les esters de l'acide itaconique avec des groupements alkyles ou oxaalkyles. L'électrolyte peut également être un liquide polaire immobilisé dans un séparateur microporeux tels qu'une polyoléfine, un polyester, des nanoparticules de silice, d'alumine ou d'aluminate de lithium LiAlO_2 . Des exemples de liquides polaires comprennent les carbonates cycliques ou linéaires, les formiate d'alkyle, les α - ω alkylethers, oligoéthylène glycols, la N-méthylpyrrolidinone, la γ -butyrolactone, les tétraalkylsulfamides, et leurs mélanges.

[0041] Les exemples suivants sont fournis afin d'illustrer certaines mises en œuvre préférentielles de l'invention, et ne doivent pas être considérés comme en limitant la portée.

Exemple 1

[0042] Cet exemple illustre la synthèse d'un matériau de l'invention conduisant directement à un matériau d'insertion recouvert d'un dépôt de carbone.

[0043] Le matériau LiFePO_4 recouvert d'un dépôt carboné a été synthétisé à partir de vivianite $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ et d'orthophosphate de lithium Li_3PO_4 en proportions stoechiométriques selon la réaction:



[0044] Une poudre de polypropylène a été ajoutée dans une proportion représentant 3 % du poids du la vivianite. Les quantités pesées de chacun des composants ainsi que la poudre de polypropylène ont été intimement broyées ensemble dans un broyeur à billes de zircone. Le mélange a ensuite été chauffé sous atmosphère inerte d'argon, dans

membrane poreuse de type Celgard™ 2400. L'électrolyte utilisé est une solution de LiTFSI 0.8 molale dans la gamma-butyrolactone.

[0051] Les voltampérogrammes présentés à la Figure 6 ont été réalisés à température ambiante avec une vitesse de balayage de 20 mV.h⁻¹ entre 3 et 3.8 volts. Dans cette configuration, les cinétiques d'oxydation et de réduction apparaissent comme étant beaucoup plus lentes qu'à 80°C. De plus, la batterie perd légèrement en puissance au cours du cyclage. En revanche, la totalité de la capacité théorique est accessible (97.5% cycle 1, 99.4% cycle 5). Elle a été échangée sans perte sur la durée de l'expérience (5 cycles). Il n'est pas exclu que la faible puissance de cette batterie puisse provenir d'une mauvaise imprégnation de l'électrode par l'électrolyte, ce dernier ne mouillant pas le polymère utilisé comme agent liant.

[0052] Cet exemple illustre donc que l'amélioration du matériau étudié, en raison de la présence du dépôt de carbone à la surface des grains, porte sur la cinétique, la capacité et la cyclabilité. De plus, son rôle est indépendant de celui du carbone ajouté lors de la préparation des cathodes composites.

Exemple 2

[0053] Cet exemple illustre la formation d'un dépôt conducteur carboné à partir d'un gaz de type hydrocarbure. La synthèse décrite dans l'exemple 1 pour la préparation du phosphate double de lithium et de fer a été reprise en omettant la poudre de polypropylène et en remplaçant l'atmosphère inerte du traitement thermique par un mélange de 1 % de propène dans l'azote. Lors du traitement thermique, le propène se décompose pour former un dépôt de carbone sur le matériau en cours de synthèse. L'échantillon obtenu contient 2.5% de carbone, déterminé par analyse chimique. Une voltammétrie cyclique réalisée dans les conditions décrites dans l'exemple 1 sur cet échantillon met en évidence un phénomène important d'activation au cours des premiers cycles (voir Figure 6). L'amélioration des cinétiques s'accompagne dans ce cas d'une augmentation de la capacité réversiblement échangée. Telle que mesurée lors de l'étape de décharge, la valeur de capacité initiale de l'échantillon de LiFePO₄ préparé représente 77% de la capacité théorique en tenant compte des 2.5 % de carbone électrochimiquement inactif. Après 5 cycles, cette capacité atteint 91.4%. Le phénomène d'activation observé est relié à l'épaisseur de la couche de carbone éventuellement poreux enrobant les grains et pouvant ralentir la diffusion des cations.

[0054] Les exemples 3-5 illustrent le traitement de l'oxyde complexe, en l'occurrence le phosphate double de fer et de lithium LiFePO₄, préparé indépendamment par voie thermique, de manière à obtenir un revêtement carboné conducteur.

Exemple 3

[0055] L'échantillon de tryphilitite LiFePO₄ tel que synthétisé précédemment a été analysé. Sa composition massique est : Fe 34.6%, Li 4.2%, P 19.2%, soit un écart à la stoechiométrie d'environ 5%. La poudre à traiter a été imprégnée d'une solution aqueuse de sucre commercial puis séchée. La quantité de solution a été choisie de manière à correspondre à 10 % du poids de sucre par rapport au poids du matériau à traiter. L'évaporation de l'eau jusqu'à sécheresse complète a été faite sous agitation pour obtenir une répartition homogène. L'emploi du sucre représente une mise en oeuvre préférentielle, car il fond avant de se carboniser, ce qui permet de bien enrober les grains. Son rendement relativement faible en carbone après pyrolyse est compensé par son prix peu élevé.

[0056] Les traitements thermiques ont été réalisés à 700°C sous atmosphère d'argon. La température a été maintenue pendant 3 heures. Une analyse élémentaire montre que ce produit contient 1.3 % en poids de carbone. Le traitement thermique précédemment décrit conduit à une poudre noire présentant une conductivité électronique de surface mesurable par un simple ohm-mètre commercial. Son électroactivité, telle que mesurée sur le 1^{er} cycle (Figure 8) et le 5^{ème} cycle (Figure 9) de charge-décharge est de 155.9 mAhg⁻¹ et 149.8 mAhg⁻¹ respectivement, soit 91.7% et 88.1% de la théorie. Ces valeurs sont à comparer à celles du produit non revêtu du dépôt carboné, dont seulement 64% sont électroactifs lors du premier cycle. Après 5 cycles, cette valeur tombe à 37.0% (voir Figure 10).

Exemple 4

[0057] Le phosphate double LiFePO₄ de l'exemple 3 a été additionné d'acétate de cellulose comme précurseur du revêtement carbone. Ce polymère est connu pour se décomposer avec de bons rendements de carbonisation, soit de l'ordre de 24 %. Il se décompose entre 200 et 400°C. Au-delà de cette température, le carbone amorphe obtenu se réorganise pour donner une structure de type graphite qui est favorable à l'obtention de dépôts de carbone cohérents et très conducteurs. L'acétate de cellulose a été dissout dans de l'acétone dans une proportion correspondant à 5 % du poids de la matière à traiter et séché avant de procéder comme décrit plus haut. La teneur du produit final en carbone est de 1.5%. Le traitement thermique conduit d'une manière similaire à un produit noir présentant une conductivité électronique de surface. Son électroactivité, telle que mesurée sur le 1^{er} cycle (Figure 8) et le 5^{ème} cycle

[0062] Le matériau recouvert du matériau carboné a été testé pour son activité électrochimique dans une pile au lithium comprenant une électrode de lithium métal, du bis-(trifluorométhanesulfonimide) de lithium 1M dans un mélange 50:50 d carbonate d'éthylène-diméthoxyéthane comme électrolyte immobilisé dans un séparateur de polypropylène microporeux de 25µm. La cathode a été obtenue à partir du matériau rédox préparé avec du noir de carbone (Ketjen-black™) et mis en pâte dans une solution du polymère d'éthylène-propylène-diène, la proportion de solides étant 85:10:5. Le mélange de la cathode est épandu sur un grillage d'aluminium expansé, et pressé à une tonne/cm² pour donner une épaisseur de 230 µm. Cet assemblage pile bouton est chargé (le matériau testé étant l'anode) à 1 mAcm⁻² entre des potentiels de 2.8 et 3.9 volts. La capacité du matériau est de 120 mAgh⁻¹, correspondant à 89% de la valeur théorique. Le potentiel moyen a été obtenu à 3.6 V vs. Li⁺:Li⁰.

Exemple 7

[0063] Cet exemple illustre l'utilisation d'un composé comprenant de l'azote comme matériau d'électrode.

[0064] Des poudres d'oxyde manganéux MnO et de nitrure de lithium, tous deux commerciaux (Aldrich), sont mélangés dans une boîte sèche sous atmosphère d'hélium dans une proportion 1:1. Les réactifs sont placés dans un creuset de carbone vitreux et traités sous atmosphère d'azote dépourvu d'oxygène (≤ 1 vpm) à 800°C. 12 g de l'oxynitrure résultante ayant une structure anti-fluorite Li₃MnNO sont ajoutés à 0.7 g d'une poudre de polyéthylène ayant des particules de l'ordre du micromètre, et mélangés dans un mélangeur à billes sous atmosphère d'hélium dans un contenant en polyéthylène avec de l'heptane sec comme agent de dispersion et 20 mg de Brij™ 35 (ICI) comme surfactant. Le mélange filtré est ensuite traité sous un courant d'azote dépourvu d'oxygène dans un four à 750°C pour décomposer le polyéthylène en carbone.

[0065] Le matériau d'électrode recouvert de carbone apparaît sous forme de poudre noire rapidement hydrolysée dans l'air humide. Toutes les manipulations subséquentes sont donc conduites dans une boîte sèche dans laquelle une pile similaire à celle de l'exemple 6 a été construite et testée pour l'activité électrochimique du matériau préparé. L'électrolyte, dans ce cas, est un mélange de tétraéthylsulfamide commercial (Fluka) et de dioxolane dans un rapport volumique 40:60. Les deux solvants ont été purifiés par distillation en présence d'hydruure de sodium (sous pression réduite de 10 torrs dans le cas de la sulfamide). À ce mélange de solvants, est ajouté le bis-(trifluorométhanesulfonimide) de lithium (LITFSI) pour former une solution de 0.85 molaire. De la même façon que pour l'exemple 6, la cellule comprend une électrode de lithium, un électrolyte immobilisé dans un séparateur en polypropylène poreux de 25 µm, et le matériau préparé de la même manière que dans l'exemple 6.

[0066] La cathode est obtenue à partir du matériau rédox préparé en mélange avec le noir de carbone (Ketjen-black™) et mis en pâte dans une solution de polymère éthylène-polypropylène-diène, la proportion de solides étant 90:5:5. Le mélange de la cathode est pressé sur un grillage de cuivre expansé à 1 tonne/cm² avec une épaisseur résultante de 125 µm. L'assemblage pile bouton est chargé à 0.5 mAcm⁻² (l'oxynitrure étant l'anode) entre des potentiels de 0.9 et 1.8 volts. La capacité des matériaux est de 370 mAgh⁻¹, i.e., 70% de la valeur théorique pour deux électrons par unité de la formule. Le potentiel moyen a été mesuré à 1.1 V vs. Li⁺:Li⁰. Ce matériau peut être utilisé comme matériaux d'électrode négative dans des piles de type lithium-ion. Une cellule expérimentale de ce type a été construite avec le matériau d'électrode sur un grillage de cuivre similaire à celui testé précédemment, et un matériau d'électrode positive obtenu par la délithiation chimique du phosphate de fer et lithium de l'exemple 1 en présence de brome dans l'acétonitrile. Le phosphate de fer (III) obtenu est pressé sur un grillage d'aluminium pour former l'électrode positive et la solution de 0.85 M de LITFSI tétraéthylsulfamide/dioxolane est utilisée comme électrolyte. Le voltage moyen de cette cellule est de 2.1 volts et sa densité d'énergie, basée sur le poids des matériaux actifs, est de 240 Wh/Kg.

Exemple 8

[0067] Le phosphosilicate de lithium vanadium (III) Li_{3.5}V₂(PO₄)_{2.5}(SiO₄)_{0.5}, ayant une structure Nasicon, est préparé de la façon suivante.

[0068] Du carbonate de lithium (13.85g), du silicate de lithium Li₂SiO₃ (6.74 g), du phosphate d'ammonium dihydrogène (43.2 g) et du vanadate d'ammonium (35.1 g) sont mélangés avec 250 mL d'éthylméthylcétone et traités dans un mélangeur à billes comprenant des billes d'alumine et un contenant de polyéthylène à parois épaisses pour 3 jours. La pâte résultante est filtrée, séchée et traitée dans un four tubulaire sous un courant d'azote comprenant 10% d'hydrogène, à 600°C pendant 12 heures. Après refroidissement, 10 g de la poudre résultante sont introduits dans un mélangeur à billes planétaires comprenant des billes de carbure de tungstène. La poudre résultante est ajoutée à une solution du polymère polyaromatique préparé à l'exemple 5 (polyoxoéthylène-co-pérylène-tétracarboxylique diimide, 0.8 g dans 5 mL d'acétone), homogénéisée, et le solvant a été évaporé.

[0069] La poudre rouge-brun a été thermolysée dans un courant d'argon dépourvu d'oxygène à 700°C pendant 2 heures, pour donner après refroidissement une poudre noire ayant une conductivité de surface mesurable. Le matériau recouvert du matériau carboné a été testé pour son activité électrochimique dans une pile lithium-ion comprenant une

s'est évaporé rapidement. La poudre résultante a été traitée sous un courant d'argon sec dépourvu d'oxygène dans un four tubulaire à 740°C pendant 3 heures, résultant en une poudre noire. L'activité électrochimique de la cellule a été testée dans une pile lithium-ion similaire à celle de l'exemple 6. L'électrolyte était, dans ce cas, l'bis-fluorométhanesulfonimide de lithium ($\text{Li}[\text{FSO}_2]_2\text{N}$) dissout à une concentration de 1 M dans le diméthylamino-trifluoroéthyl sulfamate $\text{CF}_3\text{CH}_2\text{OSO}_2\text{N}(\text{CH}_3)_2$, qui est un solvant résistant à l'oxydation. Lorsque chargée initialement, la cellule a montré une capacité de 145 mAh^{-1} dans la fenêtre de voltage 4.2 - 4.95 V vs. $\text{Li}^+:\text{Li}^0$. La batterie a pu être cyclée pendant 50 cycles de profondes charges/décharges avec moins de 10% de perte de capacité, montrant ainsi la résistance de l'électrolyte aux hauts potentiels.

Exemple 12

[0076] Le composé $\text{Li}_2\text{MnSiO}_4$ a été préparé par la calcination du gel résultant de l'action d'un mélange stœchiométrique d'acétate de lithium dihydraté, d'acétate de manganèse tétrahydraté et de tétraéthoxysilane dans un mélange éthanol/eau 80:20. Le gel a été séché dans un four à 80°C pendant 48 heures, réduit en poudre et calciné à l'air à 800°C. 3.28 g du silicate résultant et 12.62 g du phosphate de lithium et fer de l'exemple 3 sont mélangés dans un mélangeur à billes planétaire similaire à celui de l'exemple 11, et la poudre a été traitée sous un courant d'argon sec dépourvu d'oxygène dans un four tubulaire à 740°C pendant 6 heures. L'oxyde complexe obtenu après refroidissement possède la formule $\text{Li}_{1.2}\text{Fe}_{0.8}\text{Mn}_{0.2}\text{P}_{0.8}\text{Si}_{0.2}\text{O}_4$. La poudre a été humidifiée avec 3 mL d'une solution 2% d'acétate de cobalt, et séchée. Cette poudre a été traitée dans le même four tubulaire à 500°C sous un courant de 1 mL/s d'un gaz comprenant 10% de monoxyde de carbone dans de l'azote pendant 2 heures. Après refroidissement, la poudre noire résultante a été testée pour son activité électrochimique dans des conditions similaires à celles de l'exemple 1. Avec un électrolyte d'oxyde de polyéthylène à 80°C, la capacité mesurée, à partir d'une courbe cyclique de voltamogramme à 185 mAh^{-1} (88% de la théorie) entre les voltages de 2.8 et 3.9 volts vs. $\text{Li}^+:\text{Li}^0$. Le matériau non recouvert testé dans des conditions similaires possède une capacité spécifique de 105 mAh^{-1} .

Exemple 13

[0077] Sous argon, 3 g de phosphate de lithium et fer de l'exemple 3 sont suspendus dans 50 mL d'acétonitrile, auquel on ajoute 0.5 g d'hexachlorocyclopentadiène et 10 mg de tétrakis-(triphenylphosphine) nickel(0). Sous une agitation vigoureuse, 1.4 mL de tétrakis(diméthylamino)éthylène sont ajoutés goutte à goutte à la température ambiante. La solution a viré au bleu, et après l'ajout d'agent réducteur supplémentaire, au noir. La réaction est laissée sous agitation pendant 24 heures après la fin de l'addition. Le précipité noir résultant est filtré, lavé avec de l'éthanol et séché sous vide. La recuisson du dépôt de carbone a été réalisée à 400°C sous un courant de gaz dépourvu d'oxygène pendant 3 heures. La poudre noire résultante a été testée pour son activité électrochimique dans les conditions similaires à celles de l'exemple 1. La capacité mesurée entre les voltages de 2.9 et 3.7 volts vs. $\text{Li}^+:\text{Li}^0$ est de 160 mAh^{-1} (91% de la théorie). Le matériau non recouvert possède une capacité spécifique de 112 mAh^{-1} dans les mêmes conditions expérimentales.

Exemple 14

[0078] Les composés de spinelle $\text{Li}_{3.5}\text{Mg}_{0.5}\text{Ti}_4\text{O}_{12}$ ont été préparés par la technique sol-gel en utilisant le tétra(isopropoxyde) de titane (28.42 g), l'acétate de lithium dihydraté (35.7 g) et l'acétate de magnésium tétrahydraté (10.7 g) dans 300 mL d'un mélange isopropanol-eau 80:20. Le gel blanc résultant a été séché dans un four à 80°C et calciné à 800°C à l'air pendant 3 heures, ensuite sous argon comprenant 10% d'hydrogène, à 850°C pendant 5 heures. 10 g de la poudre bleue résultante sont mélangés dans 12 mL d'une solution 13% en poids d'acétate de cellulose dans l'acétone. La pâte a été séchée et le polymère carbonisé dans les conditions de l'exemple 4 sous atmosphère inerte à 700°C.

[0079] L'électrode positive d'une supercapacité électrochimique a été construite de la façon suivante: 5 g de LiFePO_4 recouvert de carbone selon l'exemple 3, 5 g de Norit® (charbon activé) 4 g de poudre de graphite (diamètre de 2 μm) 3 g de fibres d'aluminium coupées (20 μm de long et 5 mm de diamètre), 9 g de poudre d'anthracène (10 μm) comme agent formateur de pores et 6 g de polyacrylonitrile sont mélangés dans la diméthylformamide dans lequel le polymère se dissout. La pâte a été homogénéisée et enduite sur un feuillard d'aluminium (25 μm) et le solvant évaporé. Le revêtement est ensuite chauffé lentement jusqu'à 380°C sous atmosphère d'azote. L'anthracène s'évapore pour laisser place à une porosité homogène dans le matériau, et l'acrylonitrile se convertit grâce à la cyclisation thermique en un polymère conducteur comprenant des cycles pyridine fusionnés. L'épaisseur de la couche résultante est 75 μm .

[0080] Un revêtement similaire est réalisé pour une électrode négative avec un pâte dans laquelle LiFePO_4 est remplacé par le revêtement de spinelle préparé précédemment. La supercapacité est obtenue en plaçant face à face deux électrodes préparées séparées par un séparateur de polypropylène de 10 μm d'épaisseur trempé dans un mélange

vanadium, le titane, le molybdène, le niobium et le tungstène aux états d'oxydation suivants: Fe^{2+} , Mn^{2+} , V^{2+} , V^{3+} , Ti^{2+} , Ti^{3+} , Mo^{3+} , Mo^{4+} , Nb^{3+} , Nb^{4+} , W^{4+} .

5. Matériau selon la revendication 1 dans lequel le précurseur du matériau carboné comprend les hydrocarbures et leurs dérivés, le pérylène et ses dérivés, les composés polyhydriques et leurs dérivés, un polymère ou mélange de polymères, et leurs mélanges.
6. Matériau selon la revendication 5 caractérisé en ce que le précurseur comprend un polymère.
7. Matériau selon la revendication 6 caractérisé en ce que le polymère comprend les polyoléfinés, les polybutadiènes, l'alcool polyvinylique, les produits de condensation des phénols, les polymères dérivés de l'alcool furfurylique, les polymères dérivés du styrène, du divinylbenzène, de l'acrylonitrile, de l'acétate de vinyle, la cellulose, l'amidon et ses esters, et leurs mélanges.
8. Procédé de dépôt d'un matériau carboné tel que défini à la revendication 6 sur un matériau d'électrode, caractérisé en ce que le polymère ou le mélange de polymères est dispersé avec l'oxyde complexe suivi d'une pyrolyse sous vide ou sous atmosphère d'un gaz non réactif.
9. Procédé de dépôt d'un matériau carboné tel que défini à la revendication 7 caractérisé en ce qu'un monomère ou mélange de monomères est additionné à l'oxyde complexe suivi d'une polymérisation, et d'une pyrolyse effectuée sous vide ou sous atmosphère d'un gaz non réactif.
10. Procédé de dépôt d'un matériau carboné défini selon la revendication 1 caractérisé en ce que la source de carbone est le monoxyde de carbone seul ou en mélange avec un gaz inerte, et que le dépôt est obtenu par l'équilibre de dismutation $2 \text{CO} \Rightarrow \text{C} + \text{CO}_2$ à une température inférieure à 900°C optionnellement en présence d'un catalyseur.
11. Procédé de préparation d'un matériau selon la revendication 1 caractérisé en ce que le dépôt est fait par pyrolyse à partir d'un dérivé organique d'un métal alcalin A apportant la fraction a-a' du métal alcalin à partir de l'oxyde complexe $\text{A}_a\text{M}_m\text{Z}_z\text{O}_o\text{N}_n\text{F}_f$ de manière à laisser par pyrolyse un dépôt carboné à la surface de l'oxyde complexe dont la composition devient $\text{A}_a\text{M}_m\text{Z}_z\text{O}_o\text{N}_n\text{F}_f$ tel que a-a' > 0.
12. Matériau selon la revendication 1 caractérisé en ce que la teneur massique finale en matériau carboné est comprise entre 0.1 et 55%.
13. Matériau selon la revendication 1 caractérisé en ce que l'oxyde complexe comprend les sulfates, phosphates, silicates, oxysulfates, oxyphosphates, et oxysilicates, ou leurs mélanges, d'un métal de transition et de lithium, et leurs mélanges.
14. Matériau selon la revendication 1 caractérisé en ce que l'oxyde complexe est de formule $\text{Li}_{1+x}\text{MP}_{1-x}\text{Si}_x\text{O}_4$ ou $\text{Li}_{1+x-y}\text{MP}_{1-x}\text{Si}_x\text{O}_{4-y}\text{F}_y$ dans laquelle $0 \leq x, y \leq 1$ et M comprend Fe or Mn.
15. Matériau selon la revendication 1 caractérisé en ce que l'oxyde complexe est de formule $\text{Li}_{3-x-z}\text{M}_2(\text{P}_{1-x-z}\text{S}_x\text{Si}_z\text{O}_4)_3$ dans laquelle M comprend Fe ou Mn, $0 \leq x$, et $z \leq 1$.
16. Matériau selon la revendication 1 caractérisé en ce que l'oxyde complexe est de formule $\text{Li}_{3+u-x+z}\text{V}_{2-z-w}\text{Fe}_u\text{Ti}_w(\text{P}_{1-x-z}\text{S}_x\text{Si}_z\text{O}_4)_3$ ou $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$, $\text{Li}_{4+x-2y}\text{Mg}_y\text{Ti}_5\text{O}_{12}$, dans laquelle $0 \leq x$; $w \leq 2$; $y \leq 1$ and $z \leq 1$.
17. Cellule électrochimique caractérisée en ce qu'au moins une électrode comprend au moins un matériau selon la revendication 1.
18. Cellule électrochimique selon la revendication 17 caractérisée en ce qu'elle fonctionne comme batterie primaire ou secondaire, super capacité ou système de modulation de la lumière.
19. Cellule selon la revendication 18 fonctionnant comme une batterie primaire ou secondaire, caractérisée en ce que l'électrolyte est un polymère, solvant ou non, optionnellement plastifié ou gélifié par un liquide polaire contenant en solution un ou plusieurs sels métalliques.
20. Cellule selon la revendication 18 fonctionnant comme une batterie primaire ou secondaire, caractérisée en ce que

FIGURE 1

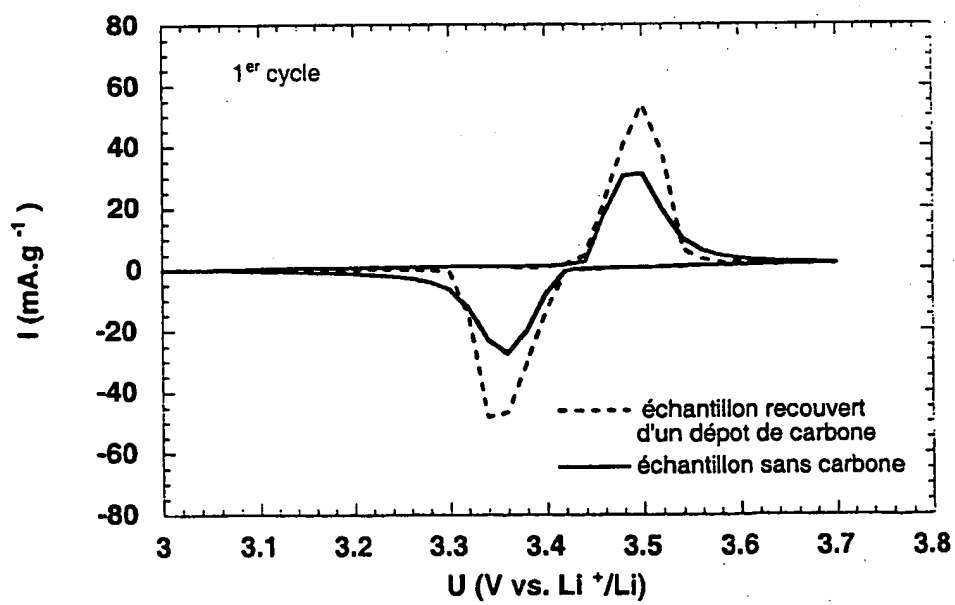
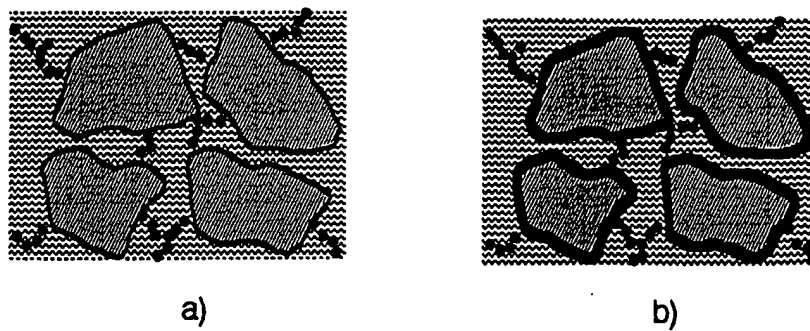


Figure 2

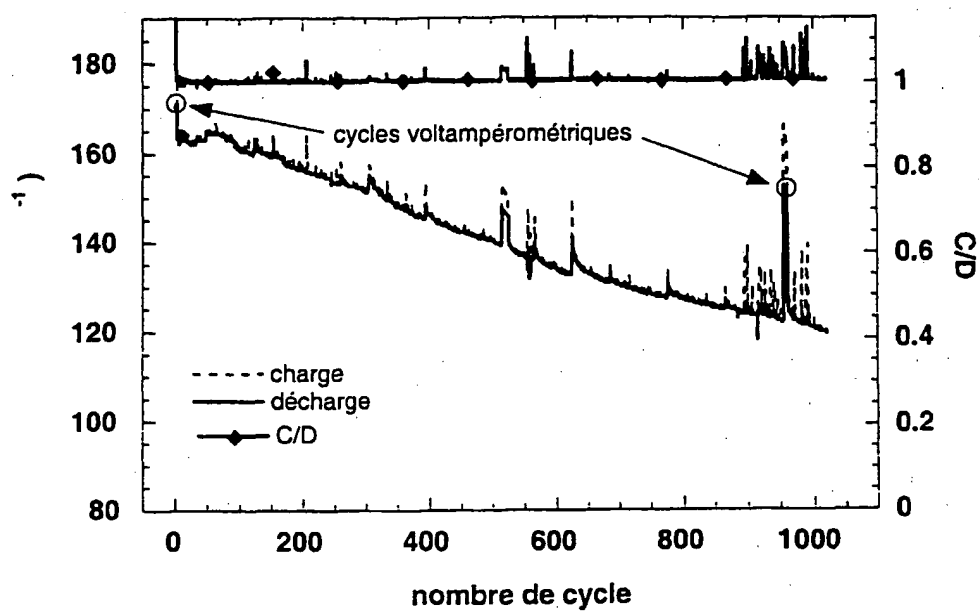


Figure 5

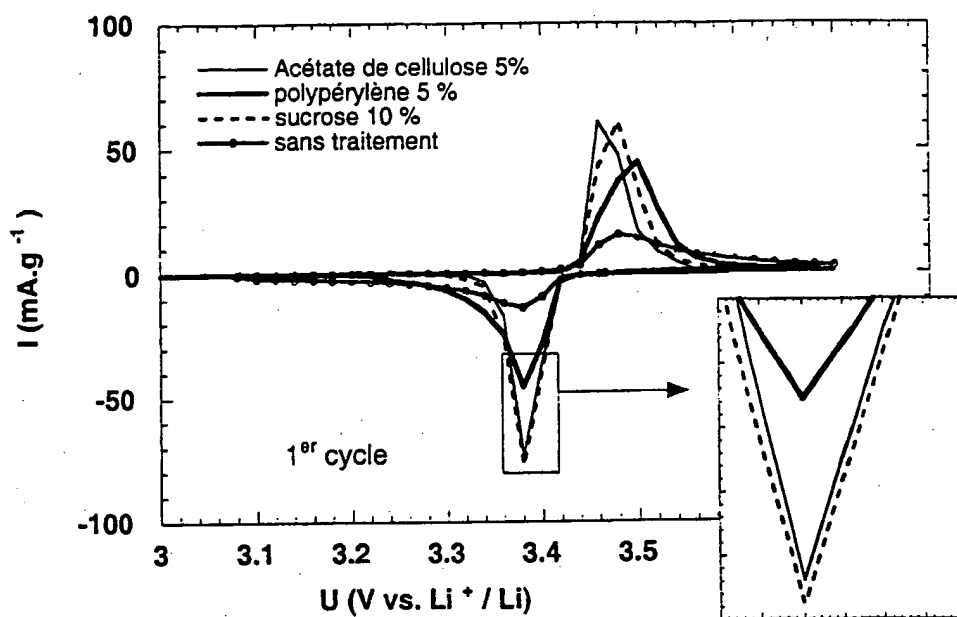


Figure 8

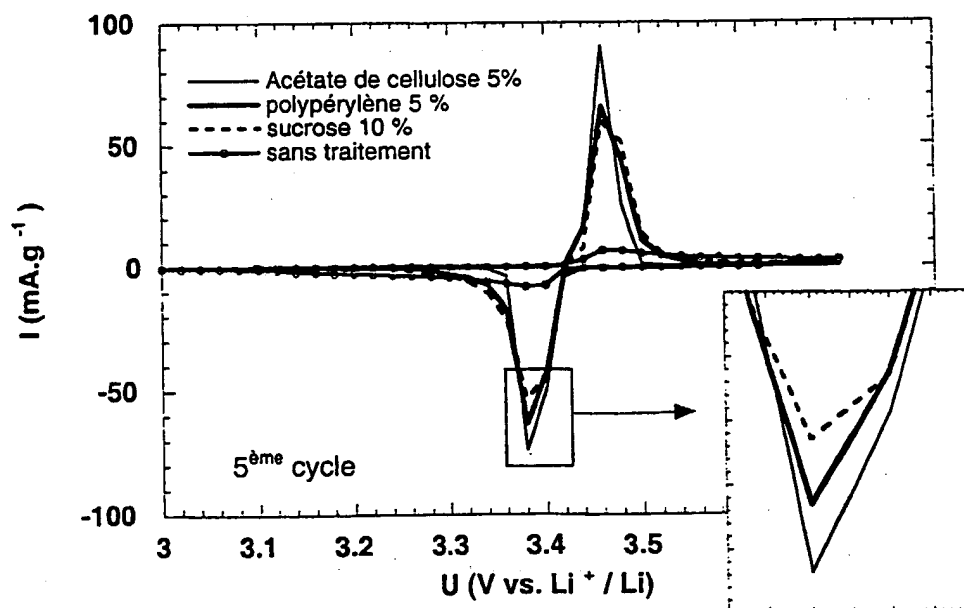


Figure 9

18

[Translation from French]

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(54) Electrode materials of high surface conductivity

(57) The present invention relates to electrode materials capable of redox reaction by alkali metal ion and electron exchange with an electrolyte. The materials are used in the domain of primary or secondary electrochemical generators (batteries), super-capacitors and supercapacitor-type light modulation systems.

FIGURE 1

Description

FIELD OF THE INVENTION

[0001] The present invention relates to electrode materials capable of redox reaction by alkali metal ion and electron exchange with an electrolyte. The materials are used in the domain of primary and secondary electrochemical generators (batteries), supercapacitors and electrochromic light modulation systems.

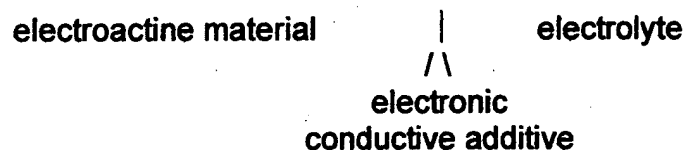
PRIOR ART

[0002] Insertion compounds (hereafter called also electroactive materials or redox materials) whose function is based on the exchange of alkali metal ions, particularly lithium ions, and of valence electrons of at least one transition element so as to ensure neutrality in the solid matrix, are known in the art. Partial or total maintenance of the structural integrity of the material permits reversibility of the reaction. The redox reactions resulting from the formation of several phases are usually not reversible, or reversible only to a very slight extent. It is also possible to carry out reactions in the solid phase by bringing into play the reversible splitting of sulfur-sulfur bonds or the redox reactions occurring during the conversion of aromatic organic structures into quinone-type forms, particularly in conjugated polymers.

[0003] The insertion materials are the active ingredients of the electrochemical reactions used particularly in electrochemical generators, supercapacitors or light transmission modulation systems (electroforms).

[0004] Progress of the ion -electron exchange reactions requires the simultaneous existence, within the insertion material, of a double conductivity by the electrons and ions, particularly lithium ions, one or the other of these conductivity types possibly being too weak to ensure the exchange kinetics required for use of the material, especially for electrochemical generators or supercapacitors. One solution of this problem is achieved, in part, by the use of so-called "composite" electrodes wherein the electrode material is dispersed in a matrix containing the electrolyte and a polymer binder. In the case where the electrode is a polymeric electrolyte or a gel functioning in the absence of solvent, the role of mechanical binder is ensured directly by the macromolecule. The term "gel" is understood to mean a polymeric matrix, itself solvating or nonsolvating, retaining a polar liquid and a salt so as to impart to the assembly the mechanical properties of a solid while retaining at least part of the conductivity of the polar solvent. A liquid electrolyte and the electrode material can also be kept in contact by a small fraction of an inert polymeric binder, i.e. one not interacting with the solvent. By any one of the aforementioned means, each grain of electrode material is thus surrounded by electrolyte capable of bringing the ions in direct contact with almost the entire electrode material surface. To facilitate the electronic exchanges, it is usual, according to the prior art, to add particles of a conductive material to one of the aforementioned mixtures of electrode material and of the electrolyte. These particles are in a highly divided state. In general, the choice falls on carbonaceous materials, and quite particularly on carbon blacks (Shawinigan or Ketjenblack^(R)). However, the volume fractions used are small because this type of material greatly modifies the rheology of the suspensions, especially of the polymers, which results in excessive porosity and loss of effectiveness

of the operation of the composite electrode in terms of both the fraction of usable capacity and of kinetics, i.e., available power. At small quantities used, the carbon grains structure themselves into chains, and the points of contact with the electrode material proper are extremely reduced. The consequence of this configuration is a bad distribution of the electrical potential within the electroactive material. In particular, excess concentrations or impoverishments may appear at the points of triple junction:



[0005] These excessive variations of the local concentration of mobile ions and the gradients resulting in the interior of the electroactive material are very injurious to the reversibility of operation of the electrode at a large number of cycles. These chemical or mechanical constraints, or stress, are reflected on the microscopic level by disintegration of the grains of the electroactive material, part of which is capable of losing contact with the carbon grains and in this way becoming electrochemically inactive. The structure of the material may also be destroyed, with the appearance of new phases and possible salting out of the derivatives or other transition metal fragments in the electrolyte. These harmful phenomena appear all the more readily as the current density or power demanded of the electrode is greater.

IN THE DRAWINGS:

[0006] Figure 1 illustrates the differences between a conventional prior-art electrode (A) and an electrode according to the invention, whose particles of electroactive material are covered by a carbonaceous coating (B).

[0007] Figures 2 and 3 show a comparison between an LiFePO_4 sample covered with carbon and a control sample of LiFePO_4 without carbon. These results were obtained by cyclic voltammetry of LiFePO_4 / $\text{POE}_{20}\text{LiTFSI}$ / Li batteries cycled at 20 mV.h^{-1} between 3 and 3.7 volts at 80°C . The first cycle is plotted in Figure 2 and the fifth cycle in Figure 3.

[0008] Figure 4 illustrates the variation of capacity in the course of cycling of batteries made of carbonaceous LiFePO_4 , on the one hand, and a non-carbonaceous control, on the other hand.

[0009] Figure 5 illustrates the performances of a battery containing carbonaceous LiFePO_4 cycled in the potentiostatic mode between 3 and 3.8 volts at 80°C with a charging/discharging rate corresponding to C/1.

[0010] Figure 6 illustrates the variation of current as a function of time of an LiFePO_4 / γ -butyrolactone LiTFSI / Li battery containing a carbonaceous sample and cycled at 20 mV.h^{-1} between 3 and 3.7 volts at room temperature.

[0011] Figure 7 illustrates the variation of current as a function of time of a LiFePO_4 / POE_{20} LiTFSI / Li battery containing a carbonaceous sample.

[0012] Figures 8 and 9 show a comparison between LiFePO_4 samples covered with carbon and a control LiFePO_4 sample before treatment. These results were obtained by cyclic voltammetry of LiFePO_4 / $\text{POE}_{20}\text{LiTFSI}$ / Li batteries cycled at 20 mC.h^{-1} between 3 and 3.7 volts at 80°C . The first cycle is shown in Fig. 8 and the fifth in Fig. 9.

[0013] Figure 10 shows the variation of capacity during cycling of batteries constructed with the carbonaceous LiFePO_4 samples on the one hand and the noncarbonaceous control, on the other hand.

SUMMARY OF THE INVENTION

[0014] The present invention relates to an electrode material comprising a complex oxide corresponding to the general formula $\text{A}_a\text{M}_m\text{Z}_z\text{O}_o\text{N}_n\text{F}_f$, wherein

A comprises an alkali metal,

M comprises at least one transition metal and optionally a metal other than a transition metal such as magnesium or aluminum or their mixtures,

Z is at least one nonmetal.

O is oxygen, N is nitrogen, and F is fluorine, and

the coefficients a, m, z, o, n and $f \geq 0$ are so chosen as to assure electroneutrality,

characterized in that a quantity of carbonaceous material is deposited on the surface of the material in a homogeneous manner in such a way as to obtain a substantially regular electric field distribution on the surface of the material grains. The similarity of the ionic radii of oxygen, fluorine and nitrogen permits mutual replacement of these elements as long as the electroneutrality is maintained. For purposes of simplification,

and considering that oxygen is used most frequently, these materials shall be called complex oxides. The preferred transition metals comprise iron, manganese, vanadium, titanium, molybdenum, niobium, zinc and tungsten, either alone or in a mixture. The preferred metals other than a transition metal comprise magnesium and aluminum, and the preferred nonmetals are copper, selenium, phosphorus, arsenic, silicon, germanium, boron and tin, used alone or in a mixture.

[0015] In a preferred embodiment, the final content of carbonaceous material is between 0.1 and 55% by mass, more preferably between 0.2 and 15%.

[0016] In another preferred embodiment, the complex oxide comprises the sulfates, phosphates, silicates, oxysulfates, oxyphosphates and oxysilicates, or their mixtures, of a transition metal and of lithium, and mixtures thereof. It may be of interest for reasons of structural stability to partially substitute the transition metal by an element of the same ionic radius but inactive from the redox point of view, for example, magnesium and aluminum in preferred proportions of 1 to 25%.

[0017] The invention also relates to an electrochemical cell wherein at least one electrode is fabricated from an electrode material according to the invention. The cell may operate as a primary or secondary battery, supercapacitor or light modulation system, the primary or secondary battery being the preferred *modus operandi*.

DETAILED DESCRIPTION OF THE INVENTION

[0018] The present invention makes it possible to prepare electrode materials of extremely varied composition which are characterized by being coated on the surface or over the major part of the surface by a uniform coating of conductive carbonaceous material deposited by chemical means. The presence of a uniform coating in the electrode materials of the invention as compared with the prior-art punctiform contact obtained with carbon powders or other conductive additives permits a regular distribution of the electric field on the surface of grains of the electroactive material. Moreover, the concentration gradients of the ions are considerably reduced. This better distribution of the electrochemical reaction on the surface of the particles makes it possible, on the one hand, to preserve the structural integrity of the material, while, on the other hand, it improves the kinetics in terms of current density and power available to the electrode, thanks to the greater surface area offered.

[0019] Understood by the term "carbonaceous material" is a solid polymer containing a preponderance of carbon (from 50 to 100 mol%) and having an electronic conductivity greater than 10^{-5} Scm^{-1} at room temperature, and preferably greater than 10^{-3} Scm^{-1} . The other elements present may be hydrogen, oxygen, nitrogen, as long as they do not interfere with the chemical inertness intrinsic to carbon during the electrochemical procedures. The carbonaceous material may be obtained by thermal decomposition or dehydrogenation, e.g. partial oxidation, of various organic compounds. In general, any material which, thanks to a reaction or sequence of reactions, leads to a solid carbonaceous material having the desirable properties without affecting the stability of the complex oxide, represents an acceptable precursor. Acceptable precursors comprise, without limitation, the

hydrocarbons and their derivatives, particularly the aromatic polycyclic species such as tar or pitch, perylene and its derivatives, polyhydric compounds such as sugars and carbohydrates, their derivatives, and polymers. Preferred polymer examples include the polyolefins, polybutadienes, polyvinyl alcohol, phenol condensation products including those obtained by reaction with aldehydes, polymers derived from furfuryl alcohol, polymers derived from styrene, from divinyl benzene, from naphthalene, from perylene, from acrylonitrile and from vinyl acetate; cellulose, starch and their esters and ethers, as well as their mixtures.

[0020] The improvement of conductivity of the surface of the grains obtained by coating them with carbonaceous material according to the present invention permits satisfactory functioning of electrodes containing electroactive materials whose electronic conductivity is insufficient to obtain acceptable performances. Complex oxides having redox couples situated in the useful voltage intervals and/or comprising inexpensive and nontoxic elements but whose conductivity is too low for practical uses become useful as electrode materials when the conductive coating is present. The choice of structures or mixtures of phases having redox properties but whose electronic conductivity is too low is much broader than that of the prior-art compounds of the type of mixed oxides of transition metals and lithium. In particular, it is possible to include in the redox structures one or more elements selected from among the nonmetals (metalloids) such as sulfur, selenium, phosphorus, arsenic, silicon or germanium, whose greater electronegativity makes it possible to modulate the redox potential of transition elements, but at the expense of electronic conductivity. A similar effect is obtained by partial or total substitution of the oxygen atoms by fluorine or nitrogen.

[0021] The electrode or redox materials are thus described by the general formula

$A_a M_m Z_z O_n F_f$ wherein

A is an alkali metal such as Li, Na or K;

M represents at least one transition metal, and optionally a metal other than a transition metal, such as magnesium or aluminum;

Z represents at least one nonmetal such as S, Se, P, As, Si, Ge;

O is oxygen;

N is nitrogen and F is fluorine, the latter elements often being able to substitute oxygen in the complex oxide due to the similar ionic radii of F^- , O^{2-} and N^{3-} ions; and each of coefficients a, m, z, o, n and f are independently ≥ 0 so as to assure the electroneutrality of the material.

[0022] The preferred oxides according to the present invention comprise those of formulas

$Li_{1+x}MP_{1-x}Si_xO_4$, $Li_{1+x-y}MP_{1-x}Si_xO_{4-y}F_y$, $Li_{3-x+z}M_2(P_{1-x-z}S_xSi_zO_4)_3$; $Li_{3+u-x+z}V_{2-z-w}Fe_uTi_w$

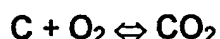
$(P_{1-x-z}S_xSi_zO_4)_3$ or $Li_{4+x}Ti_5O_{12}$, $Li_{4+x+2y}Mg_yTi_5O_{12}$, wherein $w \leq 2$; $0 \leq x$; $y \leq 1$; $z \leq 1$ and

M comprises Fe or Mn.

[0023] The carbon-containing coating may be deposited by different techniques, which form an integral part of the invention. A preferred method consists in pyrolyzing an organic material, preferably one that is rich in carbon, in the presence of the redox material.

Particularly advantageous are the mesomolecules and polymers capable of readily forming – either mechanically or by impregnation from a solution or by polymerization *in situ* – a uniform layer on the surface of the grains of the redox material. Pyrolysis or dehydrogenation

of the assembly makes it possible to obtain a fine and uniform layer of carbonaceous material on the surface of the grains of redox material. In order that the latter's composition remain unaffected by the pyrolysis or dehydrogenation reaction, it is prudent to choose compositions in which the pressure of oxygen liberated by the material is sufficiently low to avoid oxidation of the carbon formed by the pyrolysis. The activity of the oxygen of compounds $A_a M_m Z_z O_o N_n F_f$ may be controlled by the alkali metal content which itself determines the oxidation state of the transition element(s) contained in the material, and which forms an integral part of the invention. Of particular interest are the compositions wherein the coefficient "a" of the alkali metal content makes it possible to maintain the following oxidation states: Fe^{2+} , Mn^{2+} , V^{2+} , V^{3+} , Ti^{2+} , Ti^{3+} , Mo^{3+} , Mo^{4+} , Nb^{3+} , Nb^{4+} , W^{4+} . In general, oxygen pressures of the order of 10^{-20} bars at $0^\circ C$ and of 10^{-10} bars at $900^\circ C$ are sufficiently low to permit the deposition of carbon by pyrolysis, the kinetics of carbon formation in the presence of hydrocarbon residues due to the pyrolysis being faster and less strongly activated than the formation of oxygen from the redox material. It is also possible and advantageous to choose materials whose pressure of oxygen in equilibrium with the material is less than that of the equilibrium



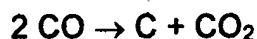
[0024] In this case, the carbonaceous material may be thermodynamically stable vis-à-vis the complex oxide. The corresponding pressures are obtained by the following formula:

$$\ln P(O_2) = \ln P(CO_2) = \frac{94050}{R(273,2 + \theta)}$$

wherein R is the perfect gas constant ($1.987 \text{ cal.mole}^{-1}, K^{-1}$), and θ is the temperature in $^\circ C$.

[0025] The following table lists the oxygen pressure values for some temperatures:

[0026] It is also possible to effect the carbon deposition by dismutation of carbon monoxide at temperatures below 800°C according to the equation:



[0027] This reaction is exothermic but slow. The complex oxide particles may be placed in contact with the pure carbon monoxide or diluted by an inert gas at temperatures between 100 and 750°C, preferably between 300 and 650°C. The reaction is advantageously carried out by the fluidized bed technique, so as to have a large exchange surface between the gas phase and the solid phase. The elements and cations of the transition metals present in the complex oxide are catalysts of the dismutation reaction. It may be of interest to add small amounts of salts of transition metals, preferably of iron, nickel, cobalt, to the surface of the grains, the salts of these elements being particularly active as catalysts of the dismutation reaction. One can also resort to the gas-phase decomposition of hydrocarbons such as the alkanes, or preferably those rich in carbon, such as alkenes, alkynes or aromatic hydrocarbons.

[0028] In one variant, the deposition of carbonaceous material can be effected simultaneously with variation of the alkali metal composition A. To do this, a salt of an organic acid or polyacid is mixed with the complex oxide. Another possibility consists in starting from a monomer or a mixture of monomers which are polymerized *in situ*. By pyrolysis, the compound deposits a film of carbonaceous material on the surface, and the alkali metal A is incorporated according to the equation



[0029] R' being any organic radical, possibly forming part of a polymeric lattice.

[0030] Among the compounds capable of permitting this reaction, mention may be made in a non-limitative manner of the salts of carboxylic acids such as the salts of oxalic, malonic, succinic, citric, polyacrylic, polymethacrylic, benzoic, phthalic, propiolic, acetylenedicarboxylic, naphthalene di- or tetracarboxylic, perylenetetracarboxylic and diphenic acids.

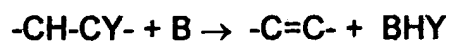
[0031] It is obvious that the pyrolysis of an organic material which does not contain an alkali metal element, and the addition of the latter through a salt, may be combined in order to arrive at the desired stoichiometry of the complex oxide.

[0032] It is also possible to obtain a deposit of carbonaceous material, especially at low or moderate temperatures below 400°C by reduction of carbon-halogen bonds according to the equation



where Y represents a halogen or pseudohalogen. Understood by the term "pseudohalogen" is an organic or inorganic radical capable of existing in the form of a Y^- ion and of forming the corresponding protonated compound HY. Among the halogens and pseudohalogens, mention may be made in a nonlimitative manner of F, Cl, Br, I, CN, SCN, CNO, OH, N_3 , RCO_2 , RSO_3 where R represents H or an organic radical. The formation by reduction of the CY bond is preferably carried out in the presence of reducing elements, e.g. hydrogen, zinc, magnesium and the Ti^{3+} , Ti^{2+} , Sm^{2+} , Cr^{2+} , V^{2+} ions, the tetrakis(dialkylaminoethylenes) or phosphines. These reagents may possibly be obtained or regenerated by an electrochemical method. Furthermore, it may be advantageous to use catalysts which increase the reduction kinetics. Particularly effective are palladium or nickel derivatives, especially in the form of complexes with phosphines, or nitrogen-containing compounds such as 2,2'-bipyridine. Similarly, these compounds can be generated in the active form by a chemical method in the presence of reducing agents, particularly those mentioned above, or by an electrochemical method. Among the compounds capable of generating carbon by reduction, mention may be made of the perhalocarbons, particularly in the form of polymers, hexachlorobutadiene, hexachlorocyclopentadiene.

[0033] Another way of liberating carbon by a low-temperature process consists in eliminating the hydrogenated compound HY, Y being as defined above, according to the equation



[0034] Among the compounds capable of generating carbon by reduction, mention may be made of organic compounds containing an equivalent number of hydrogen atoms and Y groups, compounds such as the hydrohalocarbons, particularly in the form of polymers, such as vinylidene polyfluoride, polychloride or polybromide or polyacetate, and carbohydrates. The dehydro(pseudo)halogenation may be achieved at low temperature, including room temperature, by the action of a base capable of reacting with compound HY to form a salt. In this respect, mention may be made of tertiary bases, amines, amidines, guanidines, imidazoles, inorganic bases such as alkali metal hydroxides, organometallic compounds behaving as strong bases, such as $A(N(Si(CH_3)_3)_2$, $LiN[CH(CH_3)_2]_2$ or butyl lithium.

[0035] In the last two methods mentioned above, it may be advantageous to anneal the materials after the deposit of carbon. This treatment permits an improvement of the structure or crystallinity of the carbon. The treatment may be carried out at a temperature of between 100 and 1000°C, preferably between 100 and 700°C, which makes it possible to avoid any reduction of the complex oxide by the carbonaceous material.

[0036] In a general way, it is possible to obtain uniform coatings of carbonaceous material, ensuring adequate electronic conductivity, i.e. of at least of the same order as the ionic conductivity in the oxide grain. Thick coatings make it possible to obtain a conductivity that is sufficient to ensure that the binary mixture of the complex oxide grains coated with carbonaceous material, with the liquid or polymeric electrolyte or inert macromolecular binder designed to be impregnated by electrolyte, be conductive by simple contact between

the particles. In general, this behavior may be observed at volume fractions of between 10 and 70%.

[0037] It may also be advantageous to choose deposits of carbonaceous material that is sufficiently fine so as not to obstruct the passage of ions, while ensuring the distribution of the electrochemical potential on the grain surface. In this case the binary mixtures possibly do not have an electronic conductivity that is sufficient to ensure the electronic exchanges with the electrode support (current collector). Addition of a third electronically conductive component in fine powder or fiber form makes it possible to obtain a satisfactory macroscopic conductivity and improves the electronic exchanges with the electrode support. Carbon blacks or carbon fibers are particularly advantageous for this function, and give satisfactory results at volumetric amounts which affect only slightly or not at all the rheology during the use of the electrode, due to the existence of an electronic conductivity on the surface of the grains of electrode material. Volume fractions of 0.5 to 10% are particularly preferred. Carbon blacks of the Shawinigan® or Ketjenblack® type are preferred. Among carbon fibers, those obtained by pyrolysis of polymers such as pitch, tar, polyarylonitrile, as well as those obtained by hydrocarbon cracking are preferred.

[0038] It is of interest, because of its lightness and malleability, to use aluminum as a constituent of current collectors. However, this metal is covered with an insulating oxide layer. This layer, which protects the metal against corrosion, can under certain conditions increase in thickness, which causes increased interface resistance that is harmful to th

good functioning of the electrochemical cell. This phenomenon may be particularly disturbing and rapid in the case where the electronic conductivity would, as in the prior art, be assured solely by carbon grains having a limited number of contact points. The use, in conjunction with aluminum, of electrode materials covered by a layer of carbonaceous conductive layer makes it possible to increase the aluminum-electrode exchange surface. In this way the effects of aluminum corrosion are annulled or at least significantly minimized. It is possible to use aluminum collectors either in the form of strips or, possibly, in the form of expanded metal, which permits a weight gain. Because of the properties of the materials of the invention, even in the case of an expanded metal, the electronic exchanges at the collector take place without notable increase of resistance.

[0039] When the current collectors are thermally stable, it is also possible to carry out the pyrolysis or dehydrogenation directly on the collector so as to obtain, after deposition of carbon, a continuous porous film which can be infiltrated by an ionic conductive liquid or by a monomer or monomer mixture whose *in situ* polymerization generates a polymeric electrode. Formation of porous films in which the carbonaceous coating forms a lattice is readily achieved within the framework of the invention by pyrolysis of a polymer-complex oxide composite deposited in the film state on a metallic support.

[0040] During the use of the electrode material of the present invention in an electrochemical cell, preferably of the primary or secondary battery type, the electrolyte is preferably a solvating or nonsolvating polymer that is optionally plastified or gelified by a polar liquid containing one or more metal salts in solution, preferably at least one lithium salt.

In such case, the polymer is preferably formed of units of oxyethylene, oxypropylene, acrylonitrile, vinylidene fluoride, acrylic or methacrylic acid esters, esters of itaconic acid with alkyl or oxaalkyl groups. The electrolyte can also be a polar liquid immobilized in a macroporous separator such as a polyolefin, a polyester, nano-particles of silica, alumina or lithium aluminate LiAlO_2 . Examples of polar liquids include cyclic or linear carbonates, alkyl formate, α - ω alkyl ethers, oligoethylene glycols, N-methylpyrrolidinone, γ -butyrolactone, tetraalkylsulfamides, and mixtures thereof.

[0041] The following examples are given in order to illustrate certain preferential uses of the invention, and should not be considered as limiting the scope thereof.

Example 1

[0042] This example illustrates the synthesis of a material of the invention which leads directly to an insertion material covered with a carbon deposit.

[0043] The material LiFePO_4 covered with a carbonaceous deposit was synthesized from vivianite $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ and lithium orthophosphate Li_3PO_4 in stoichiometric proportions, according to the reaction



[0044] A polypropylene powder was added in an amount of 3% by weight of vivianite.

The weighed quantities of each of the components as well as the polypropylene powder were intimately ground in a mill with zircon balls. The mixture was then heated in an inert argon

atmosphere in a first stage at 350°C for 3 hours to dehydrate the vivianite, then the temperature was gradually increased to 700°C to crystallize the material and carbonize the polypropylene. The temperature was maintained at 700°C for 7 hours. The structure of the resulting material was verified by X-ray analysis and corresponds to that published for triphylite. The percent of carbon present in the sample was determined by elementary analysis. At the precision of measurement, the carbon content is 0.58% in the example presented. For comparison, a sample was prepared under the same conditions but by omitting the polypropylene. This sample also shows a pure crystalline structure of the type of LiFePO_4 .

Electrochemical properties

[0045] The materials prepared were tested in type CR 2032 button batteries at room temperature and at 80°C.

Test at 80°C

[0046] The cathodes were prepared by mixing the powder of active material with carbon black (Ketjenblack[®]) to assure the electronic exchange with the current collector and with polyethylene oxide of mass 400,000 used as binder, on the one hand, and ionic conductor, on the other hand. The weight proportions are 95 : 9 : 56. Acetonitrile is added to the mixture in order to dissolve the polyethylene oxide. The homogenized mixture is then poured on a stainless steel disk of 1.7 cm². The cathode is dried in vacuum, then transferred to a Vacuum Atmosphères glove box under a helium atmosphere (< 1 vpm H₂O, O₂). A lithium foil (27 μm) laminated onto a nickel substrate was used as anode.

The polymeric electrolyte consisted of polyethylene oxide of mass 5,000,000 and of LiTFSI (lithium salt of bis-trifluoromethanesulfonimide) in an oxygen (of oxy thyl ne units) / lithium ratio of 20 : 1.

[0047] The electrochemical experiments were carried out at 80°C, the temperature at which the ionic conductivity of the electrolyte is sufficient ($2 \times 10^{-3} \text{ Scm}^{-1}$). The electrochemical tests were done by slow voltammetry (20 mV.h^{-1}) controlled by a Macpile^(R) type battery cycler. The batteries were charged and discharged between 3.7 and 3 volts.

[0048] Figure 2 shows the first cycle obtained for the carbonaceous and noncarbonaceous materials whose synthesis is described above. For the noncarbonaceous sample, the oxidation and reduction phenomena extend over a broad range of potentials. For the carbonaceous material, the peaks are better defined. The course of the two materials during the first 5 cycles is very different (Figure 3). For the sample covered with a carbon deposit, the oxidation and reduction kinetics are more and more rapid, which is reflected by increasingly better defined peaks (currents of higher peaks and narrower peaks). In turn, for the noncarbonaceous sample, the kinetics appear increasingly slower. The course of the capacity of these two samples is shown in Figure 4. For the carbonaceous sample the exchanged capacity is stable. According to the tests, it represents 94 to 100% of the theoretical capacity (170 mAh.g^{-1}). The initial capacity of the noncarbonaceous material is around 145 mAh.g^{-1} , or 85 % of the theoretical capacity. For this sample, the exchanged capacity decreases rapidly. After 5 cycles, the battery has lost 20 % of its initial capacity.

[0049] The carbonaceous sample was cycled in the potentiostatic mode between 3.8 and 3 V with rapid charge and discharge regimes. The corresponding imposed currents correspond to a C/1 regimen, which means that all the capacity is exchanged in 1 hour. These cycling results are shown in Figure 5. The first five cycles were carried out in voltamperometric mode in order to activate the cathode and determine its capacity. In this case, 100% of the theoretical capacity was exchanged during the first voltammetric cycle and 96% during the first 80 potentiostatic cycles. Subsequently, the capacity slowly decreases, and after 1000 cycles, 70% of the capacity (120 mAh.g^{-1}) is still exchanged in this regime. Cycling in the potentiodynamic mode carried out after 950 cycles shows that, in fact, 89% of the initial capacity is still available at slower discharge regimes. This loss of power is associated with an increase of the lithium / polymeric electrolyte interface resistance. The erratic course of the C/D parameter (capacity passed in charge) / (capacity passed in discharge) at the end of cycling makes one presume that dendrites are formed. This parameter is plotted in Figure 5.

Test at room temperature (liquid electrolyte)

[0050] The material LiFePO_4 covered with a carbon deposit was also tested at room temperature. In this case, the composite cathode is prepared by mixing the active material with carbon black and EPDM (previously dissolved in cyclohexane) in a ratio of 85 : 5 : 10. The mixture is spread on a stainless steel current collector in the form of a disk of 1.7 cm^2 , dried in vacuo and stored in a glove box under a helium atmosphere. As in the preceding case, lithium is used as anode. The two electrodes are separated by a Celgard™ 2400-type porous membrane. The electrolyte used is a 0.8 molal solution of LiTFSI in γ -butyrolactone.

[0051] The voltamperograms shown in Figure 6 were recorded at room temperature at a sweep rate of 20 mV.h^{-1} between 3 and 3.8 volts. In this configuration, the oxidation and reduction kinetics appear to be much slower than at 80°C . Moreover, the battery loses power to a slight extent during cycling. In turn, all of the theoretical capacity is accessible (cycle 1: 97.5 %, cycle 5: 99.4 %). It was exchanged without loss over the duration of the experiment (5 cycles). It is not ruled out that the low power of this battery may be due to poor impregnation of the electrode with the electrolyte, the latter not wetting the polymer used as binder.

[0052] Thus, this example shows that improvement of the material under study involves the kinetics, capacity and cyclability, thanks to the presence of the carbon deposit on the grain surface. Moreover, the latter's role is independent of that of the carbon added during the preparation of the composite cathodes.

Example 2

[0053] This example shows the formation of a carbonaceous conductive deposit from a hydrocarbon-type gas. The synthesis described in Example 1 for the preparation of the lithium-iron double phosphate was repeated but by omitting the polypropylene powder and replacing the inert atmosphere of the heat treatment by a mixture of 1% propene in nitrogen. During the heat treatment, the propene decomposes to form a carbon deposit on the material during the synthesis. The sample obtained contains 2.5% carbon, determined by chemical analysis. Cyclic voltammetry carried out on this sample under the conditions described in Example 1 reveals an important activation phenomenon during the first cycles

(see Figure 6). In this case, improvement of the kinetics is accompanied by an increase of the reversibly exchanged capacity. As measured during the discharge stage, the value of initial capacity of the prepared LiFePO_4 sample represents 77% of the theoretical capacity, taking into account the 2.5% electrochemically inert carbon. After 5 cycles, this capacity attains 91.4%. The observed activation phenomenon is related to the thickness of the possibly porous carbon layer surrounding the grains and may slow the diffusion of the cations.

[0054] Examples 3 to 5 illustrate the treatment of the complex oxide, in the present case the iron-lithium double phosphate LiFePO_4 , prepared independently by a thermal method so as to obtain a conductive carbonaceous coating.

Example 3

[0055] The previously synthesized sample of triphylite LiFePO_4 was analyzed. Its mass composition is: Fe 34.6%, Li 4.2%, P 19.2%, representing an approximately 5% deviation from stoichiometry. The powder to be treated was impregnated with an aqueous solution of commercial sucrose, then dried. The amount of solution was chosen to correspond to 10% by weight of the sucrose relative to the material to be treated. Evaporation of the water to complete dryness was done with agitation in order to obtain a homogeneous distribution. The use of sugar represents a preferred use, because it melts before being carbonized, which makes it possible to coat the grains well. Its relatively low yield of carbon after pyrolysis is compensated by its low price.

[0056] The heat treatment was carried out at 700°C under an argon atmosphere. The temperature was maintained for 3 hours. Elementary analysis shows that the product contains 1.3% by weight of carbon. The heat treatment described above leads to a black powder having an electronic surface conductivity that can be measured by means of a simple commercial ohm-meter. Its electroactivity, as measured in the first cycle (Figure 8) and fifth charge-discharge cycle (Figure 9), is 155.9 mAhg⁻¹ and 149.8 mAhg⁻¹, respectively, or 91.7% and 88.1% of the theoretical. These values should be compared with those of the product not coated with a carbonaceous deposit, of which only 64% are electroactive during the first cycle. After 5 cycles, this value falls to 37.0% (see Figure 10).

Example 4

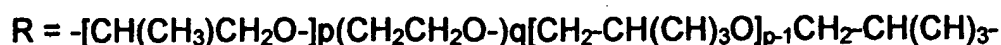
[0057] To the double phosphate LiFePO₄ of Example 3 was added cellulose acetate as precursor of the carbon coating. This polymer is known for decomposing with good carbonization yields (of the order of 24%). It decomposes between 200 and 400°C. Beyond this temperature, the resulting amorphous carbon reorganizes to give a graphite-type structure which is favorable to obtaining coherent and highly conductive carbon deposits. The cellulose acetate was dissolved in acetone in a proportion corresponding to 5% by weight of the material to be treated, and dried before proceeding as described above. The carbon content of the final product is 1.5%. The heat treatment leads, in a similar manner, to a black powder having an electronic surface conductivity. Its electroactivity, as measured in the first cycle (Figure 8) and fifth charge-discharge cycle (Figure 9) is 152.6 mAhg⁻¹ and 150.2 mAhg⁻¹, respectively, or 89.8% and 88.3% of the theoretical. These values should be compared with those of the product not coated with carbonaceous deposit,

only 64% of which are electroactive during the first cycle. After 5 cycles, this value falls to 37.0% (see Figure 10).

Example 5

[0058] Perylene and its derivatives are known to give, after pyrolysis, graphite-type carbons due to the existence of condensed rings in the starting molecule. In particular, perylenetetracarboxylic anhydride decomposes above 560°C to give carbon coatings of high covering power. However, this product is present in a state of very low solubility, and its intimate mixing with the complex oxide – in this case also, LiFePO_4 according to Example 3 – is difficult to carry out in practice. To solve this problem, a polymer was synthesized in a first step containing the perylene groups separated by an ethylene polyoxide chain. The oxyethylene segments are chosen to be sufficiently long in order to act as solubilizing agents of the aromatic groups in the usual organic solvents. To do this, the anhydride of commercial 3,4,9,10-perylenetetracarboxylic acid (Aldrich) is reacted with Jeffamine 600 (Hunstmann, USA) at elevated temperature, according to the reaction

with



$$1 \leq p \leq 2; 10 \leq n \leq 14$$

The synthesis was carried out for 48 hours in dimethylacetamide at reflux (188°C). The polymer formed is precipitated in water, then separated by filtration. It is purified by dissolution in acetone, filtration, followed by reprecipitation from ether. This process makes it possible to eliminate the unreacted starting products and small masses. Finally, the resulting powder is dried. The yield of carbonization of this product is of the order of 20%.

[0059] This polymer was dissolved in dichloromethane in a proportion corresponding to 5% of the weight of the material to be treated, before proceeding as described in Examples 3 and 4. The carbon content of the final product is 1%. The heat treatment leads, as above, to a black conductive powder. Its electroactivity, as measured in the first cycle (Figure 8) and fifth charge-discharge cycle (Figure 9) is 148 mAhg^{-1} and 146.9 mAhg^{-1} , or 87.4% and 86.4% of the theoretical. These values should be compared with those of the product not coated with carbonaceous deposit, only 64% of which are electroactive during the first cycle. After 5 cycles, this value falls to 37.9% (see Figure 10).

Example 6

[0060] This example illustrates the use of a reaction of elimination from a polymer to form a carbonaceous deposit according to the present invention.

[0061] Ferric sulfate $\text{Fe}_2(\text{SO}_4)_3$ having an orthorhombic "Nasicon" structure is obtained from commercial iron (III) sulfate hydrate (Aldrich) by dehydration at 450°C in vacuum.

By cooling and with agitation, the powder is suspended in hexane and lithiated with a stoichiometric amount of 2 M butyl lithium to give the composition $\text{Li}_{1.5}\text{Fe}_2(\text{SO}_4)_3$. 20 g of this white power is suspended in 100 mL of acetone; 2.2 g of polyvinylidene bromide $(-\text{CH}_2\text{CBr}_2)_n$ is added and the mixture is processed for 12 hours in a ball mixer containing alumina balls. The resulting suspension is dried in a rotary evaporator and ground in a mortar to give a crude powder. The solid is treated with 3 g of diazabicyclo[5.4.0]undec-7-ene (DBL) in acetonitrile under reflux for 3 hours. The black powder thus obtained is filtered to remove the amine bromide and excess reagent, rinsed with acetonitrile and vacuum-dried at 60°C . The carbonaceous deposit is annealed under an atmosphere of argon devoid of oxygen (< 1 ppm) at 400°C for 3 hours.

[0062] The material covered with the carbonaceous matter was tested for its electrochemical activity in a lithium battery comprising an electrode of lithium metal, 1 M lithium bis-(trifluoromethanesulfonimide) in a 50:50 mixture of ethylene carbonate and dimethoxyethane as electrolyte immobilized in a microporous polypropylene separator of $25\ \mu\text{m}$. The cathode was obtained from a redox material prepared with carbon black (KetjenblackTM) and made into a paste in a solution of ethylene-propylene diene polymer, the proportion of solids being 85 : 10 : 5. The cathode mixture is spread on an expanded aluminum grid and pressed at a pressure of one ton per cm^2 to a thickness of $230\ \mu\text{m}$. This button battery assembly is charged (the material tested being the anode) at $1\ \text{mAcm}^{-2}$ between the potentials of 2.8 and 3.9 volts. The capacity of the material is $120\ \text{mAhg}^{-1}$, corresponding to 89% of the theoretical value. The mean potential was obtained at 3.6 V vs. $\text{Li}^+ : \text{Li}^0$.

Example 7

[0063] This example illustrates the use of a compound comprising nitrogen as electrode material.

[0064] Manganous oxide (MnO) powder and lithium nitride powder (both of them commercially available [Aldrich]) were mixed in a dry box under an atmosphere of helium in a 1 : 1 ratio. The reagents are placed in a vitreous carbon crucible and treated in an atmosphere of nitrogen devoid of oxygen (≤ 1 vpm) at 800°C. 12 g of the resulting oxynitride having an antifluorite structure Li_3MnNO are added to 0.7 g of a polyethylene powder having micrometer-order particles, and mixed in a ball mixer in a polyethylene container under a helium atmosphere with dry heptane as dispersant and 20 mg of BrijTM 35 (ICI) as surfactant. The filtered mixture is then treated under a stream of nitrogen devoid of oxygen in a furnace of 750°C, to decompose the polyethylene into carbon.

[0065] The electrode material covered with carbon appears in the form of black powder that is rapidly hydrolyzed in humid air. Hence, all subsequent manipulations are carried out in a dry box in which a battery similar to that of Example 6 had been constructed and tested for electrochemical activity of the prepared material. In this case, the electrolyte is a mixture of commercial tetraethylsulfamide (Fluka) and dioxolane in a volume ratio of 40 : 60. The two solvents were purified by distillation in the presence of sodium hydride (at a reduced pressure of 10 torr in the case of the sulfamide). To this solvent mixture is added lithium bis-(trifluoromethanesulfonimide)

(LiTFSI) to form an 0.85 molar solution. In the same way as in Example 6, the cell comprises a lithium electrode, an electrolyte immobilized in a porous polypropylene separator of 25 μm , and the material is prepared in the same manner as in Example 6.

[0066] The cathode is obtained from redox material prepared in a mixture with carbon black (Ketjenblack™) and made into a paste in a solution of ethylene-polypropylene-diene polymer, the ratio of the solids being 90 : 5 : 5. The cathode mixture is pressed on a grid of expanded copper at a pressure of 1 ton/cm² to a resulting thickness of 125 μm . The button battery assembly is charged at 0.5 mAcm⁻² (the oxynitride tested being the anode) at 1 mAcm⁻² between the potentials of 0.9 and 1.8 volts. The capacity of the material is 370 mAgh⁻¹, i.e. 70% of the theoretical value for two electrons per unit of the formula. The mean potential was measured at 1.1 V vs. Li⁺ : Li⁰. This material may be used as a negative electrode material in lithium ion-type batteries. An experimental cell of this type was constructed with the electrode material on a copper grid similar to the previously tested one, and a positive electrode material obtained by chemical delithiation of the iron-lithium phosphate of Example 1 in the presence of bromine in acetonitrile. The resulting iron (III) phosphate is pressed on an aluminum grid to form the positive electrode, and the 0.85 M solution of LiTFSI tetraethylsulfamide / dioxolane is used as electrolyte. The average voltage of this cell is 2.1 volts and its energy density based on the weight of active materials is 240 Wh/kg.

Exempl 8

[0067] The lithium vanadium (III) phosphosilicate $\text{Li}_{3.5}\text{V}_2(\text{PO}_4)_{2.5}(\text{SiO}_4)_{0.5}$, having a Nasicon structure, is prepared as follows.

[0068] Lithium carbonate (13.85 g), lithium silicate Li_2SiO_3 (6.74 g), ammonium dihydrogen phosphate (43.2 g) and ammonium vanadate (35.1 g) are mixed with 250 mL of ethyl methyl ketone and treated for 3 days in a ball mixer comprising alumina balls and a thick-walled polyethylene container. The resulting paste is filtered, dried and treated in a tubular furnace under a stream of nitrogen containing 10% hydrogen, at 600°C for 12 hours. After cooling, 10 g of the resulting powder is introduced into a planetary ball mixer comprising tungsten carbide balls. The resulting powder is added to a solution of polyaromatic polymer prepared in Example 5 (polyoxoethylene-copolymerenetetra-carboxylic diimide, 0.8 g in 5 mL of acetone), homogenized, and the solvent was evaporated.

[0069] The red-brown powder was thermolysed in a stream of argon devoid of oxygen at 700°C for 2 hours, to give, after cooling, a black powder having a measurable surface conductivity. The material covered with the carbonaceous material was tested for its electrochemical activity in a lithium ion battery comprising a natural graphite electrode (NG7) covered with a copper current collector, and corresponding to 24 mg/cm^2 of 1 M lithium hexafluoro-phosphate in a 50 : 50 mixture of ethylene carbonate: dimethyl carbonate as electrolyte immobilized in a microporous polypropylene separator of 25 μm . The cathode was obtained from a lithium vanadium

phosphosilicate redox material mixed with carbon black (Ketjenblack™) and made into a paste with a solution of a copolymer of vinylidene fluoride and hexafluoropropene in acetone, the solids ratio being 85 : 10 : 5. The cathode mixture is spread on a grid of expanded aluminum and pressed at a pressure of 1 ton/cm², resulting in a thickness of 190 μm, corresponding to a load of active material of 35 mg/cm². The button battery assembly (the material tested being the anode) is charged at 1 mAcm⁻² between the potentials of 0 and 4.1 volts. The capacity of the material covered with carbon is 184 mAgh⁻¹, which corresponds to 78% of the theoretical value (3.5 lithium per unit of formula), with a slight decrease after cycling. By way of comparison, a similar cell constructed by using a non-covered material such as obtained after mixing heat-treated inorganic precursor but omitting the addition of perylene polymer shows a capacity of 105 mAgh⁻¹, which rapidly decreases with cycling.

Example 9

[0070] This example illustrates the formation of a carbonaceous coating by varying the alkali metal content in the redox material.

[0071] 13.54 g of commercial iron (III) fluoride (Aldrich), 1.8 g of hexa-2,4-dyinedicarboxylic acid lithium salt are mixed in a ball mixer comprising a thick-walled polyethylene container and alumina balls, in the presence of 100 mL of acetonitrile. After 12 hours, the resulting paste is filtered and the dried powder is treated with a stream of dry nitrogen devoid of oxygen in a tubular furnace at 700°C for 3 hours.

According to elementary analysis, the resulting black powder contains 47% Fe, 46% F, 1.18% Li and 3.5% C, which corresponds to the formula $\text{Li}_{0.2}\text{FeF}_3\text{C}_{0.35}$. The electrode material was tested for its capacity in a cell similar to that of Example 6, with the difference that the cell is first tested in discharge (the electrode material being the cathode), and then recharged. The voltages were between 2.8 and 3.7 volts. The experimental capacity during the first cycle was 190 mAgh^{-1} , which corresponds to 83% of the theoretical values. By comparison, a cell with FeF_3 as electrode material and no carbonaceous coating has a theoretical capacity of 246 mAgh^{-1} . In practice, the first discharge cycle obtained under conditions similar to those of the material of the invention is 137 mAgh^{-1} .

very similar to p

Example 10

[0072] This example illustrates also the formation of a carbon coating by varying the alkali metal content of the redox material.

[0073] Commercial polyacrylic acid of molecular weight 15,000 was dissolved to give a 10% solution in a water / methanol mixture, and titrated with lithium hydroxide at pH 7. Then $4 \mu\text{L}$ of this solution was dried in a crucible with thermogravimetric air at 80°C to evaporate the water / methanol. The heating was continued at 500°C , giving a residue of 0.1895 mg of calcined lithium carbonate.

[0074] 18.68 g of commercial iron (III) fluoride dihydrate (Aldrich), 8.15 g of lithium oxalate (Aldrich), 39 mL of a solution lithium polyacrylate, 80 mL of acetone and 40 mL of 2,2-dimethoxyacetone capable of trapping the water by chemical reaction, are mixed in a ball mixer comprising a thick-walled polyethylene bottle and alumina balls. After 24 hours, the resulting paste is filtered and dried. The resulting powder is treated with a stream of dry nitrogen devoid of oxygen in a tubular furnace at 700°C for 3 hours, yielding a blackish powder. According to elementary analysis, the resulting black powder contains 34% Fe, 18.8% P, 4.4% Li and 3.2% C. X-ray analysis confirmed the existence of pure triphylite LiFePO_4 as the sole crystalline compound. The electrode material was tested for its capacity in a cell similar to that of Example 1 with a polyethylene oxide electrolyte, and then recharged. The voltages were chosen between 2.8 and 3.7 volts. The experimental capacity during the first cycle was 135 mAh^{-1} , which corresponds to 77% of the theoretical value, and which increases to 156 mAh^{-1} (89%) when the definition of the peak improves after several cyclings. 80% of this capacity is accessible within the potential range of 3.3 – 3.6 volts vs. $\text{Li}^+ : \text{Li}^0$.

Example 11

[0075] The compound $\text{LiCo}_{0.75}\text{Mn}_{0.25}\text{PO}_4$ was prepared by intimately grinding cobalt oxalate dihydrate, manganese oxalate dihydrate and ammonium dihydrogen phosphate by injecting air of 850°C for 10 hours. The resulting mauve powder is mixed in a planetary ball mixer containing tungsten carbide balls, until particles of the order of

4 μm are obtained. 10 g of this complex phosphate is triturated in a mortar with 10 mL of a 6% perylene polymer solution of Example 5 in methyl formate. The solvent evaporates rapidly. The resulting powder was treated under a stream of dry argon devoid of oxygen in a tubular furnace at 740°C for 3 hours, giving a black powder. The electrochemical activity of the cell was tested in a lithium ion battery similar to that of Example 8. In this case, the electrolyte was lithium bis-fluoromethanesulfonimide ($\text{Li}[\text{FSO}_2]_2\text{N}$) dissolved at 1 M concentration in dimethylaminotrifluoroethyl sulfamate $\text{CF}_3\text{CH}_2\text{OSO}_2\text{N}(\text{CH}_3)_2$, which is a solvent resistant to oxidation. When initially charged, the cell showed a capacity of 145 mAh^{-1} in the voltage window of 4.2 – 4.95 V vs. Li^+/Li^0 . The battery could be cycled for 50 cycles of deep charges / discharges with less than 10% loss of capacity, thus showing the resistance of the electrolyte at high potentials.

Example 12

[0076] The compound $\text{Li}_2\text{MnSiO}_4$ was prepared by calcining the gel resulting from the action of a stoichiometric mixture of lithium acetate hydrate, manganese acetate tetrahydrate and tetraethoxysilane in an 80 : 20 mixture of methanol / water. The gel was dried in a furnace at 80°C for 48 hours, reduced to powder and calcined in air at 800°C. 3.28 g of the resulting silicate and 12.62 g of lithium iron phosphate of Example 3 are mixed in a planetary ball mixer similar to that of Example 11, and the powder was treated under a stream of dry argon devoid of oxygen in a tubular furnace at 740°C for 6 hours. The complex oxide obtained after cooling has the formula

$\text{Li}_{1.2}\text{Fe}_{0.8}\text{Mn}_{0.2}\text{P}_{0.6}\text{Si}_{0.2}\text{O}_4$. The powder is wetted with 3 mL of a 2% cobalt acetate solution, and dried. This powder was treated in the same tubular furnace at 500°C under a stream of 1 mL/s of gas containing 10% carbon monoxide in nitrogen for 2 hours. After cooling the resulting black powder was tested for its electrochemical activity under conditions similar to those of Example 1. With an electrolyte of polyethylene oxide at 80°C the capacity measured from a cyclic voltammogram curve [is] 185 mAgh^{-1} (88% of theory) between voltages 2.8 and 3.9 volts vs. $\text{Li}^+ : \text{Li}^0$. The non-covered material tested under similar conditions has a specific capacity of 105 mAgh^{-1} .

Example 13

[0077] Under argon, 3 g of lithium iron phosphate of Example 3 is suspended in 50 mL of acetonitrile to which are added 0.5 g of hexachlorocyclopentadiene and 10 mg of nickel (0) tetrakis-(triphenylphosphine). Under vigorous agitation, 1.4 mL of tetrakis (dimethylamino)ethylene is added in a dropwise manner at room temperature. The solution turned blue, and after the addition of supplementary reducing agent, it became black. The reaction is left under agitation for 24 hours after the end of the addition. The resulting black precipitate is filtered, washed with ethanol and vacuum-dried. Annealing of the carbon deposit was done at 400°C under a stream of gas devoid of oxygen for 3 hours. The resulting black powder was tested for its electrochemical activity under conditions similar to those of Example 1. The capacity measured between the voltages of 2.9 and 3.7 volts vs. $\text{Li}^+ : \text{Li}^0$ is 160 mAgh^{-1} (91% of theory).

The non-covered material has a specific capacity of 112 mAh^{-1} under the same experimental conditions.

Example 14

[0078] The spinel compounds $\text{Li}_{3.5}\text{Mg}_{0.5}\text{Ti}_4\text{O}_{12}$ were prepared by the sol-gel technique using titanium tetra(isopropoxide) (28.42 g), lithium acetate dihydrate (35.7 g) and magnesium acetate tetrahydrate (10.7 g) in 300 mL of an 80 : 20 mixture of isopropanol / water. The resulting white gel was dried in a furnace at 80° and calcined at 800°C for 3 hours, then, under argon containing 10% hydrogen, at 850°C for 5 hours. 10 g of the resulting blue powder is mixed with 12 mL of a solution of 13% by weight of cellulose acetate in acetone. The paste was dried and the polymer carbonized under the conditions of Example 4 in an inert atmosphere at 700°C .

[0079] The positive electrode of an electrochemical supercapacitor was constructed in the following manner: 5 g of LiFePO_4 covered with carbon according to Example 3, 5 g of Norit® (activated carbon), 4 g of graphite powder ($2 \mu\text{m}$ diameter), 3 g of cut aluminum fibers ($20 \mu\text{m}$ long and 5 mm in diameter), 9 g of anthracene powder ($10 \mu\text{m}$) as pore-forming agent and 6 g of polyacrylonitrile are mixed in dimethylformamide in which the polymer dissolves. The paste was homogenized, coated on an aluminum foil ($25 \mu\text{m}$) and the solvent was evaporated. The coating is then slowly heated to 380°C under a nitrogen atmosphere. The anthracene evaporates, to leave a homogeneous porosity in the material, and the acrylonitrile converts, thanks to thermal cyclization, into

a conductive polymer comprising fused pyridine rings. The thickness of the resulting layer is 75 μm .

[0080] A similar coating is prepared for a negative electrode with a paste in which LiFePO_4 is replaced by the spinel coating prepared above. The supercapacitor is obtained by placing face to face two prepared electrodes separated by a 10 μm thick polypropylene separator soaked in a 1 M mixture of LiTFSI in a 50 : 50 composition of acetonitrile and dimethoxyethene. This system may be charged at 30 mAcm^{-2} and 2.5 V, and produces a specific power of 3KW/L^{-1} at 1.8 V.

Example 15

[0081] A light modulation system (electrochrome window) was constructed in the following manner.

[0082] The LiFePO_4 of Example 3 is mixed in a high-energy ball mixer until obtaining particles of approximately 120 nm. 2 g of this powder is mixed with 1 mL of a solution of 2% by weight of the perylene-copolyoxyethylene polymer of Example 5 in methyl formate. The paste is triturated in order to assure a uniform distribution of the polymer on the surface of the particles, and solvent is then evaporated. The resulting dry powder is treated, under a stream of dry nitrogen devoid of oxygen, in a tubular furnace at 700°C for 3 hours, to obtain a pale gray powder.

[0083] 1 g of this powder covered with carbon is made into a paste with a solution of 1.2 g of polyethylene-c-(2-methylene)propane-1,3-diyl prepared according to *J. Electrochem. Soc.* 1994, 141 (7), 1915, with segments of ethylene oxide of molecular weight 1000, 280 mg of LiTFSI and 15 mg of diphenylbenzyl dimethyl acetal as photoinitiator in 10 mL of acetonitrile. The solution was coated by a doctor-blade process on a glass covered with an indium tin oxide ($20\text{S}^{-1}\square$) to a thickness of 8 μm . After evaporation of the solvent, the polymer was polymerized with a UV lamp of 254 nm (200 mWcm^{-2}) for 3 minutes.

[0084] Tungsten trioxide was deposited by thermal evaporation on another glass covered with indium tin oxide (ITO) to a thickness of 340 μm . This system was obtained by depositing an electrolyte layer of polyethylene oxide (120 μm) with LiTFSI at an oxygen (of the polymer) / salt ratio of 12 previously coated on a polypropylene foil and applied to an electrode covered with WO_3 by using the adhesive transfer technology. The two glass electrodes were pressed together to form the electrochemical chain:

glass / ITO / WO_3 / PEO-LiTFSI / LiFePO_4 composite electrode / ITO / glass.

[0085] This system turns blue in 30 seconds upon application of a voltage (1.5 V, the LiFePO_4 side being the anode) and whitens upon inverse voltage. The light transmission is modulated from 85% (whitened state) to 20% (colored state).

[0086] Although the present invention was described by means of specific applications, it is understood that several variations and modifications may be inserted thereinto, and the present application aims at covering these modifications, uses or adaptations of the present invention which generally follow the principles of the invention and include any variation of the present invention which will become known or conventional in the field of activity of the present invention, and which may be applied to the essential elements mentioned above, in accordance with the scope of the following claims.

Claims

1. Electrode material comprising a complex oxide corresponding to the general formula $A_aM_mZ_zO_oN_nF_f$ wherein
A comprises an alkali metal,
M comprises at least one transition metal and optionally a metal other than a transition metal, such as magnesium or aluminum or their mixtures,
Z is at least one nonmetal.
O is oxygen, N is nitrogen and F is fluorine, and
the coefficients a, m, z, o, n and $f \geq 0$ being so chosen as to assure electroneutrality, characterized in that a quantity of conductive carbonaceous material is deposited on the surface of the material in a homogeneous manner in such a way as to obtain a substantially regular electric field distribution on the surface of the material grains.
2. Material according to Claim 1, characterized in that the carbonaceous material is deposited by pyrolysis of an organic material.
3. Material according to Claim 1 characterized in that the transition metal comprises iron, magnesium, vanadium, titanium, molybdenum, niobium, zinc and tungsten, used alone or in mixture, the metal other than transition metal comprises magnesium or aluminum, and the nonmetal comprises sulfur, selenium, phosphorus, arsenic, silicon, germanium, boron and tin, used alone or in mixtures.

4. Material according to Claim 3, characterized in that the transition metal comprises iron, manganese, vanadium, titanium, molybdenum, niobium and tungsten in the following oxidation states: Fe^{2+} , Mn^{2+} , V^{2+} , V^{3+} , Ti^{2+} , Ti^{3+} , Mo^{3+} , MO^{4+} , Nb^{3+} , Nb^{4+} , W^{4+} .
5. Material according to Claim 1 in which the precursor of carbonaceous material comprises the hydrocarbons and their derivatives, perylene and its derivatives, polyhydric compounds and their derivatives, a polymer or polymer mixture, and mixtures thereof.
6. Material according to Claim 5, characterized in that the precursor comprises a polymer.
7. Material according to Claim 6, characterized in that the polymer comprises the polyolefins, polybutadienes, polyvinyl alcohol, phenol condensation products, polymeric derivatives of furfuryl alcohol, polymers derived from: styrene, divinylbenzene, acrylonitrile, vinyl acetate, cellulose, starch and its esters, and mixtures thereof.
8. Process for the deposition of a carbonaceous material such as defined in Claim 6, on an electrode material, characterized in that the polymer or mixture of polymers is dispersed with the complex oxide, followed by pyrolysis carried out in vacuum or in an atmosphere of nonreactive gas.

9. Process for the deposition of a carbonaceous material such as defined in Claim 7, characterized in that a monomer or monomer mixture is added to the complex oxide, followed by polymerization and by pyrolysis carried out in vacuum or in an atmosphere of nonreactive gas.
10. Process for the deposition of a carbonaceous material defined according to Claim 1, characterized in that the source of carbon is carbon monoxide alone or in a mixture with an inert gas, and the deposit is obtained by the dismutation equilibrium $2 \text{ CO} \rightarrow \text{C} + \text{CO}_2$ at a temperature below 900°C , optionally in the presence of a catalyst.
11. Process for the preparation of a material according to Claim 1, characterized in that the deposit is produced by pyrolysis of an organic derivative of an alkali metal A supplying the fraction $a-a'$ of the alkali metal from the complex oxide $\text{A}_a\text{M}_m\text{Z}_z\text{O}_o\text{N}_n\text{F}_f$ so as to leave by pyrolysis a carbonaceous deposit on the surface of the complex oxide whose composition becomes $\text{A}_a\text{M}_m\text{Z}_z\text{O}_o\text{N}_n\text{F}_f$ such that $a-a' > 0$.
12. Material according to Claim 1, characterized in that the final carbonaceous material content by mass is between 0.1 and 55%.

13. Material according to Claim 1, characterized in that the complex oxide comprises the sulfates, phosphates, silicates, oxysulfates, oxyphosphates or oxysilicates, or their mixtures, of a transition metal or lithium, and mixtures thereof.
14. Material according to Claim 1, characterized in that the complex oxide has the formula $\text{Li}_{1+x}\text{MP}_{1-x}\text{Si}_x\text{O}_4$ or $\text{Li}_{1+x-y}\text{MP}_{1-x}\text{Si}_x\text{O}_{4-y}\text{F}_y$ wherein $0 \leq x$, $y \leq 1$, and M comprises Fe or Mn.
15. Material according to Claim 1, characterized in that the complex oxide has the formula $\text{Li}_{3-x+z}\text{M}_2\text{P}_{1-x-y}\text{S}_x\text{Si}_z\text{O}_4)_3$ wherein M comprises Fe or Mn, $0 \leq x$, and $z \leq 1$.
16. Material according to Claim 1, characterized in that the complex oxide has the formula $\text{Li}_{3+u-x+z}\text{V}_{2-z-w}\text{Fe}_u\text{Ti}_w(\text{P}_{1-x-z}\text{S}_x\text{Si}_2\text{O}_4)_3$ or $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$, $\text{Li}_{4+x-2y}\text{Mg}_y\text{Ti}_5\text{O}_{12}$ wherein $0 \leq x$, $w \leq 2$, $y \leq 1$ and $z \leq 1$.
17. Electrochemical cell, characterized in that at least one electrode comprises at least one material according to Claim 1.
18. Electrochemical cell according to Claim 17, characterized in that it functions as a primary or secondary battery, supercapacitor or light modulation system.

19. Cell according to Claim 18 functioning as a primary or secondary battery, characterized in that the electrolyte is a solvating or nonsolvating polymer, optionally plastified or gelified by a polar liquid containing one or more metallic salts in solution.
20. Cell according to Claim 18 functioning as a primary or secondary battery, characterized in that the electrolyte is a polar liquid immobilized in a microporous separator.
21. Cell according to Claim 19, wherein one of the metallic salts is a lithium salt.

[Glossary to text in Figures 1 to 10:]

French

English

<i>Echantillon recouvert d'un dépôt de carbone</i>	= Sample covered with a carbon deposit
<i>Echantillon sans carbone</i>	= Sample without carbon
<i>nombre de cycle</i>	= cycle number
<i>capacité</i>	= capacity
<i>cycles voltamperométriques</i>	= voltamperometric cycles
<i>décharge</i>	= discharge
<i>Acétate de cellulose 5%</i>	= 5% cellulose acetate
<i>polypérylène 5%</i>	= 5% polyperylene
<i>sans traitement</i>	= without treatment
<i>1^{er} cycle</i>	= first cycle